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RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

No. II.

THE ACTION OF BROMINE ON TOLUOL, AND SOME OF ITS DERIVATIVES.*

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The history of the action of halogens on toluol begins with the discovery of toluol by Pelletier and Walter, who say in their paper,† published in 1838, on "retinnaphte" (toluol) from coal tar, that by distilling it repeatedly in a stream of chlorine there was formed a brownish-yellow oil with a sharp taste, a very strong smell somewhat like that of horse-radish, and a powerful action on the eyes, whose formula, founded on a doubtful analysis, was $C_7H_6Cl_2$, and which with potassic hydrate gave potassic chloride and an oil with a different smell. They also tried the action of bromine on boiling retinnaphte, and made in this way a compound similar to the preceding in every respect, but they observed that the cold hydrocarbon was apparently unaffected by chlorine.

* Presented to the American Academy of Arts and Sciences. Communicated by the Authors.

† Ann. Chim. Phys. 67, 269.

Deville* was the next to take up the subject in 1841, in his paper on balsam of tolu, from which he obtained a hydrocarbon (benzoene) identical with the retinnaphte of Pelletier and Walter. From this he made the following compounds: C_7H_7Cl, boiling point 170°, by the action of chlorine on the hydrocarbon when cooled and protected from light; $C_7H_6Cl_4$ in diffused daylight; $C_7H_5Cl_7$ when the chlorine was in excess; $C_7H_6Cl_8$ in direct sunlight; and $C_7H_5Cl_9$ by repeated distillation in an atmosphere of chlorine.

The next important step was taken by Cannizzaro† in 1855, who proved that the product of the action of chlorine on toluol is identical with benzylchloride made from benzylalcohol. Beilstein,‡ in 1860, introduced a great deal of confusion into the subject by contradicting Gerhardt's§ inference from Deville's work, that the action of chlorine on cold toluol was different from its action on hot, and describing experiments of his own to prove that differences in temperature made no difference in the products. He also thought he had proved the identity of the dichlortoluol from toluol and chlorine with the chlorobenzol made from benzaldehyde with phosphoric pentachloride, but Cahours,‖ three years later (1863), announced that they were only isomeric. In the same year (1863), Naquet¶ studied trichlortoluol in comparison with the product of the action of phosphoric pentachloride on benzylchloride.

The next important discovery was made in 1865 by Fittig and Glinzer,** who obtained monobromtoluol by treating cold toluol with bromine, and pointed out the marked differences between it and chlortoluol (benzylchloride); while in 1866 Kekulè,†† in his paper on aromatic isomeres described benzylbromide made from benzylalcohol, and, after comparing it with monobromtoluol, explained the cause of their difference.

In this same year (1866), Beilstein, in conjunction with Geitner,‡‡ put the whole subject on a firm basis by the following statement, since known as *Beilstein's Law:— Toluol behaves differently with chlorine according as it is hot or cold;* in the cold, a chlortoluol as stable as chlorbenzol is formed, usually, however, mixed with benzylchloride unless great care is taken in cooling. If hot, the toluol is converted into benzylchloride, but it is not necessary absolutely to boil it, as a very slight increase of temperature is enough com-

* Ann. Chim. Phys. ser. 3, 3, 178.
† Ann. Chem. Pharm. 96, 246.
‡ Traité de Chimie, 3, 567.
§ Ibid. 116, 336.
‖ Comptes rendus, 56, 222.
¶ Ibid. 55, 407; 56, 129.
** Ann. Chem. Pharm. 133, 47; 136, 301.
†† Ibid. 137, 188.
‡‡ Ibid. 139, 331.

pletely to prevent the formation of chlortoluol. *With iodine only chlortoluol is formed under all conditions, even when the toluol is boiling;** the chlortoluol obtained by this process is however contaminated with substances containing iodine. In this paper they predict a similar action with bromine, and state that xylol behaves with chlorine like toluol. A paper by Limpricht† in the same volume of the *Annalen der Chemie und Pharmacie*, and another by Cannizzaro‡ in the next volume but one, did not advance the subject materially.

Lauth and Grimaux§ in 1867, described a convenient form of the process for making benzylchloride, consisting in passing chlorine into toluol heated to 110–140° in a flask with a return condenser. In the same year, Beilstein‖ extended his law to the action of bromine on toluol, which, if iodine was present, gave bromtoluol as the only product with the exception of a little of some iodine compound, even if the toluol was boiling, while without iodine bromine formed with boiling toluol benzylbromide, always, however, mixed with some bromtoluol. Lauth and Grimaux,¶ on the other hand, could find no bromtoluol in the product obtained by mixing the vapors of bromine and toluol.

Since that time but little progress has been made in this subject, the papers in which the action of halogens on toluol is mentioned dealing rather with the products than with the conditions of the action, but the following papers deserve mention: Fittig,** on the formation of bromtoluol free from benzylbromide; Beilstein and Kuhlberg,†† extending Beilstein's Law to the action of chlorine on the various chlorine compounds of toluol, and one of their later papers‡‡ (on tetrachlortoluol) in which they direct that 2 or 3 grams of iodine should be used to make the chlorine enter the ring. This is the only statement of the amount of iodine needed for this purpose that we have been able to find, and even here nothing is said of the amount of toluol to be used with the 3 grams of iodine.

We have not been more successful in finding definite statements about the temperature at which the bromine begins to enter the side-chain. Those authors§§ who mention any temperature give the

*The use of iodine was suggested by the paper of H. Müller (Journal London Chem. Soc. 15, 41) on making chlorine substitution products from benzol in presence of iodine.

†Ann. Chem. Pharm. 139, 303. ‡Ibid. 141, 198. §Ibid. 143, 79. ‖Ibid. 143, 369.

¶Bull. Chem. Soc. 7, 108. **Ann. Chem. Pharm. 147, 39.

††Ibid. 146, 317; also 147, 339. ‡‡Ibid. 150, 286.

§§Vogt and Henninger, Ann. Chim. Phys. ser. 4, 27, 130. Grimaux Comptes rendus, 7[illegible] 1363. Radziszewski, Ber. d. ch. G. 1873, p. 492.

boiling point of the substance to be acted on, or a temperature somewhat above this, with the exception of Wachendorff,* who in studying the action of bromine on para- and metanitrotoluol, found that the benzylbromine was formed as low as 130° in a sealed tube, or at 180° in open vessels, while at its boiling point the nitrotoluol was almost entirely decomposed by bromine.

In the work described in this paper we have tried to give a more definite statement to Beilstein's law,—which may be stated thus: When toluol (or its derivatives) is treated with chlorine or bromine in the cold, the halogen attaches itself to the benzol ring; if hot, to the side-chain; in presence of iodine exclusively to the ring, even when boiling.—To do this we have tried to determine the amount of benzylbromide formed from toluol and some of its derivatives, in the first place at different temperatures, and secondly in presence of different amounts of iodine.

Effect of Differences in Temperature.

In these experiments a weighed amount of toluol or the substituted toluol was heated in a flask with a return condenser by a paraffine bath, and the calculated quantity of bromine added with a drop-funnel at such a rate that no bromine could be seen in the fumes which escaped through the condenser. The temperature of the bath and of the vapor within the flask was noted throughout the experiment. To determine how much benzylbromide had been formed we used the following method, which is very similar to that used by Cannizzaro† for the same purpose. The product of the reaction, after being freed from hydrobromic acid by washing first with a dilute solution of sodic carbonate and afterwards with distilled water, was heated to 100° with alcoholic ammonia for two hours; the bromides of ammonium and the three benzylamines thus formed were decomposed by warming with a solution of baric hydrate, and the amount of baric bromide determined by Volhard's‡ sulphocyanate method of titration after the organic matter had been filtered off. To test the method of estimating the amount of removable bromine, pure parabrombenzylbromide was treated with alcoholic ammonia and baric hydrate, as described above, and 98 per cent. of the calculated amount of bromine obtained. The experiments collected in Table I. were then made.

* Ann. Chem. Pharm. 185, 259. † Ibid. 141, 198. ‡ Ibid. 190, 1.

TABLE I.

ACTION OF BROMINE ON TOLUOL. BOILING-POINT, 111°.

Number of Experiment.	Amount taken.	Temperature.		Per cent. of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
I.	5 grs.	100°	97°–98°	72.	65
II.	5 grs.	100°	98°–100°	54.	20
III.	10 grs.	100°	97°–98°	55.	60
IV.	10 grs.	100°	95°	65.	55
V.	5 grs.	120°	110°–114°	82.	10
VI.	10 grs.	120°	112°–114°	87.	20
VII.	10 grs.	120°	111°–113°	74.	20

ACTION OF BROMINE ON PARACHLORTOLUOL. MELTING-POINT, 7°; BOILING-POINT, 160°.

Number of Experiment.	Amount Taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
VIII.	6.9 grs.	100°	81°–86°	69.	45
IX.	"	120°	110°–113°	80.	
X.	"	140°	130°–135°	92.	20
XI.	"	167°	157°–161°	95.	15

ACTION OF BROMINE ON PARABROMTOLUOL. MELTING-POINT, 28.5°; BOILING-POINT, 185°.

Number of Experiment.	Amount taken.	Temperature.		Per cent. of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
XII.	9.4 grs.	100°	87°–92°	51.	
XIII.	"	100°	90°–93°	58.	40
XIV.	"	120°	111°–114°	95.	25
XV.	"	120°	110°–114°	90.	30
XVI.	"	140°	130°–134°	88.	10
XVII.	"	170°	160°–164°	92.	8
XVIII.	"	190°	180°–184°	94.	5

ACTION OF BROMINE ON ORTHOBROMTOLUOL. BOILING-POINT, 182°.

Number of Experiment.	Amount taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
XIX.	9.4 grs.	100°	90°	21.	30
XX.	"	100°	86°–92°	31.	45
XXI.	"	100°	90°	32.	55
XXII.	"	1 0°	110°–114°	74.	50
XXIII.	"	140°	130°–134°	83.	25
XXIV.	"	170°	160°–164°	84.	10
XXV.	"	190°	180°–184°	84.	15

Before considering the inferences which can be drawn from these results, it is necessary to examine the sources of error which affect the accuracy of the process; and, for this purpose, all the results obtained under the same conditions are collected in Table II.

TABLE II.

No. of Experiment.	Time in Minutes.	Per cent.
TOLUOL AT 100°. 5 grs. used.		
I.	65	72
II.	20	54
TOLUOL AT 100°. 10 grs. used.		
III.	60	55
IV.	55	65
TOLUOL AT 120°. 5 grs. used.		
V.	10	82
TOLUOL AT 120°. 10 grs. used.		
VI.	20	87
VII.	20	74
PARABROMTOLUOL AT 120°.		
XIV.	25	95
XV.	30	90
ORTHOBROMTOLUOL AT 100°.		
XIX.	30	21
XX.	45	31
XXI.	55	32

The want of agreement between these results can be ascribed to two causes: first, differences in the rate of adding the bromine; second, unavoidable defects in the method of bromiring or of treating the product. To the first class belong the difference of 18 per cent., corresponding to 45 minutes difference in rate between Nos. I. and II., and that of 10 per cent., corresponding to 15 minutes between Nos. XIX. and XX.; but these are the only differences that come under this class, a difference of less than 10 minutes having apparently no effect upon the amount of benzylbromide formed (see XX. and XXI.). The differences due to the second cause are that of 10 per cent. between III. and IV., 13 per cent. between VI. and VII., and 5 per cent. between XIV. and XV., which show that our method is incapable of giving the exact quantitative results that we had hoped for. The most probable cause of these variations is the difficulty of washing and handling the liquid or pasty product of the bromiring. In the following discussion, Experiment I. will be rejected, because of the very slow rate at which the bromine was added, and differences of less than 10 per cent. will be accepted, if at all, only with greatest caution.

Effect of the Temperature on the Amount of Benzylbromide formed.—To make this comparison easier, the results given in

Table I. (reduced to the mean where there are several observations at the same temperature) are collected in the following table, and in the second column, under each substance, the differences between the percentages at each temperature, and at that which immediately follows it, are given.

TABLE III.

Temperature.	Toluol.		Parachlortoluol.		Parabromtoluol.		Orthobromtoluol.	
	Per cent.	Difference.	Per cent.	Difference.	Per cent.	Difference.	Per cent.	Difference.
81°–100°	58	23	69	11	54	38	28	46
110°–114°	81		80	12	92	−4	74	9
130°–135°			92	3	88	4	83	1
160°–164°			95		92	2	84	0
180°–184°					94		84	
110°–Bpt.				15		2		10

From this it appears that the bromine begins to enter the side-chain in considerable quantity at about the boiling point of toluol (111°), and that after this the amount of benzylbromide formed increases with the temperature, although to a much smaller extent, with the exception of parabromtoluol, which is probably due to defects in the process; in fact, the difference between 81°–100° and 110°–114° is greater than that between the latter temperature and the boiling point of the substance, except in the case of the single series of observations on parachlortoluol.

Some experiments with paraiodtoluol cannot be directly compared with the preceding, because we could find no satisfactory way of removing the iodine set free during the addition of the bromine, and were therefore obliged to content ourselves with weighing the crystals of paraiodbenzylbromide formed. We found, under these conditions, that below 100° no crystals were formed; at about 111°, 18 per cent. of the calculated amount was obtained; at 135°, 42 per cent.; at 175°, 54 per cent.; at 200°, 51 per cent. The low percentages are partly accounted for by the solubility of the paraiodbenzylbromide in the oily secondary products. A similar series with parachlortoluol gave below 100° no crystals; at 111°, 89 per cent. of very impure crystals (apparently nearly one-half parachlor-

toluol); at 135°, 98 per cent. of purer crystals; at 160°, 89 per cent. These results confirm, in a general way, those obtained by the more accurate method.

The effect of differences in temperature on the rate at which the bromine is taken up will be seen from the following table, in which the mean time needed to convert into the bromine product equivalent weights of the substances for each temperature is given. In calculating these means, the times of several experiments were used, in which the amount of benzylbromide was not determined; many of them, therefore, depend on a much larger number of observations than the mean amounts given in Table III.

TABLE IV.

Temperature.	Time in Minutes.			
	Toluol.	Parachlortoluol.	Parabromtoluol.	Orthobromtoluol.
81°–100°	26	40	43	43
110°–114°	11	30	27	40
130°–135°		22	10	25
160°–164°		20	8	10
180°–184°			5	15

Although the method of adding the bromine used by us made great differences of rate, under the same conditions, possible, so that all these results must be taken with some caution, it is evident that the rate increases rapidly, and apparently regularly, with the temperature, showing no especially large increase between 81°–100° and 110°–114°, as was the case with the per cent. This rapid increase in the rate suggests the following objection to the results obtained in studying the effect of temperature on the amount of benzylbromide formed; the small percentages of benzylbromide obtained below 100° may have been due to loss of bromine from running the experiment too fast, as the secondary products were not studied; and therefore it is possible that they were the unaltered original substance, and not formed from this by substitution of bromine in the ring; this view is supported by the larger per cent. (72) obtained in Experiment I., where the time was 45 minutes longer than in II.; but, on the other hand, it is hardly possible that nearly 5 grams of bromine could have escaped without giving a perceptible color to about the same quantity of hydrobromic acid, and great pains were taken in every experiment to regulate the addition of

the bromine so that the escaping fumes should be perfectly colorless. Even if the amounts of benzylbromide obtained below 100° are rejected on this account, our statement that there is a decided change in the action at 111° still holds good, as in that case the time necessary to take up the bromine below 100° must be greatly increased, and therefore the differences in rate between 87°–100° and 110°–114° would become as great in proportion to the differences between other temperatures as those in the percentages are if our present results are accepted.

We had hoped, in beginning this research, to make a careful comparison of the action of bromine on toluol and its substitution products, but the differences between the results from different substances fall so near the wide limits of error of our process, that we prefer to confine ourselves to the following very general statements. Bromine is taken up by toluol more rapidly than by any of its substitution products studied; orthobromtoluol seems to take up bromine less rapidly than parabromtoluol, and this inference from our quantitative results is confirmed by our experience in the preparation of the substituted benzylbromides in large quantity, when it has been observed invariably that the parabromtoluol absorbed bromine most rapidly, the meta-compound less so, and the orthobromtoluol even more slowly than the meta. In regard to the percentages of benzylbromide formed from each substance we do not feel that our results allow us to make any generalization, as the apparently lower numbers obtained from the orthobromtoluol may be due to differences in working up the product, which in the case of the ortho-compound is a liquid, while the parabromtoluol yields a pasty solid.

We have also tried some experiments with toluol at lower temperatures, and found that at 58°, and even at 0°, a small amount of benzylbromide was formed, as shown by obtaining an amine on treatment of the product with alcoholic ammonia. The rate at which the bromine was taken up was, however, extremely slow, and we feel that these experiments need confirmation.

Effect of the Addition of Iodine.

We were induced to take up this branch of the subject by the observation that paraiodbenzylbromide was formed by the action of bromine on paraiodtoluol, even when the flask was filled with violet vapors of iodine during the addition of the bromine, which

contradicted Beilstein's Law as generally understood; but we have not studied it so thoroughly as the effect of differences in temperature, as we could find no sufficiently satisfactory and easy method of determining the amount of benzylbromide formed.

Our best series of results (Table V.) was obtained from parachlortoluol treated with bromine at 160°, the crystals of parachlorbenzylbromide formed being weighed after they had been brought to the melting point of the pure substance, 48.5°.

TABLE V.

Per cent. of Iodine added.	10 grs. Parachlortoluol yielded.	Per cent of possible Amount.
1	6.5 grs.	51
5	3. grs.	23
10	No crystals.	

The product of the last experiment was washed, boiled with alcoholic sodic acetate, and then heated in a sealed tube with aqueous ammonia, when crystals of the parachlorbenzylalcohol were obtained, showing that even in presence of 10 per cent. of iodine a portion of the bromine enters the side-chain. This result was confirmed by some experiments on toluol, in one of which toluol was mixed with 10 per cent. of iodine and treated with chlorine at 120°; on fractioning the product, about one-half passed over from 164°–222° (chlortoluol boils from 156°–160°), attacked the mucous membrane of the nose violently, and gave an amine when heated in a sealed tube with alcoholic ammonia; it must, therefore, have contained benzylchloride (boiling point 176°), and probably chlorbenzylchloride (boiling point 213°). In another experiment it seemed that even 40 per cent. of iodine was not enough to completely prevent the formation of benzylbromide at 111°; but the determination of the benzylbromide by the amine process was interfered with by the presence of iodine substitution products to such an extent that we can place but little reliance on this result.

Summary.

I. The portion of Beilstein's Law which states that benzyl-compounds are formed at high, and substituted toluols at low temperatures, is confirmed by our experiments.

II. The benzyl-compound begins to be the principal product near the boiling point of toluol (111°); in other words, no connection can be traced between the boiling point of a substituted toluol and the temperature at which the bromine begins to enter its side-chain in quantity. Above 111° there is a gradual increase in the amount formed as the temperature is raised; but the total increase from 111° to the boiling point of the substance is usually smaller than the increase from 100° to 111°.

III. The rate at which the bromine is taken up becomes more rapid as the temperature is raised.

IV. Toluol takes up bromine more rapidly than its substitution products. This result is confirmed by the observation of Beilstein and Kuhlberg,* that the more chlorine there was attached to the ring, the harder it was to introduce chlorine into the side-chain.

V. The monobromtoluols seem to take up bromine (in the side-chain) in the following order: para most rapidly, meta next, ortho least rapidly.

VI. The portion of Beilstein's Law which states that in presence of iodine no benzyl-compound is formed, even at the boiling point, is not true when the amount of iodine is 10 per cent. or less, and it is probable that toluol yields a little benzylbromide at 111°, even in presence of 40 per cent. of iodine.

From our experiments it follows that the best way to obtain a benzylbromide is to add the bromine at the boiling point of the substance used, but it is not well to allow the temperature to rise above this point, as then there is danger of decomposition of the product.

ON α- AND β-MONOBROMCROTONIC ACIDS.

By Arthur Michael and Lewis M. Norton.

Aug. Kekulè,† in his researches on non-saturated organic acids, found that citradibrompyrotartaric acid when heated with an aqueous alkaline solution decomposed, forming carbonic, hydrobromic and a monobromcrotonic acid, and that the latter acid gave on reduction with nascent hydrogen butyric acid. A short time

* Ann. Chem. Pharm. 150, 286. † Ann. Chem. Pharm. Suppl. 2, 97.

later, A. Cahours* obtained, by the action of bromine on potassium citraconate, a dibrombutyric acid, which on boiling with alkalis decomposed into hydrobromic and the bromcrotonic acid of Kekulè. It is evident that these acids are of the greatest importance in ascertaining the constitution of citraconic acid, and with this object in view W. Körner† endeavored to obtain them synthetically from solid crotonic acid, by subjecting it to the action of bromine, and treating the dibrombutyric acid thus formed with alkalis. Körner only published a preliminary notice of his results, in which he states that the monobromcrotonic acid thus obtained is in every respect identical with the acid of Kekulè. Bulk‡ has also examined the action of bromine on solid crotonic acid, and obtained a solid compound which he considered as either dibromcrotonic or -butyric acid; his analytical results indicate the formation of the first compound. It would appear from the results obtained by Kekulè and Körner that the bromo-acid is a derivative of solid crotonic acid, but the later investigations of Geromont§ and Swarts,‖ who reduced this acid and found it yielded isobutyric acid, of Morawski¶ and of Fittig and Prehn** have shown that this conclusion is erroneous, and that it must be considered as a monobrommethacrylic acid. Körner's results, therefore, appear extremely interesting, since to explain the identity of the two monobromo-acids a molecular rearrangement of bromcrotonic into brommethacrylic acid must be supposed. We considered this subject of sufficient interest to repeat Körner's experiments, and examine his bromcrotonic acid more thoroughly.

β-Monobromcrotonic Acid.

This acid is the product of the action of alcoholic potash upon *αβ*-dibrombutyric acid.††

The dibrombutyric acid was obtained in the following manner: solid crotonic acid was dissolved in a large quantity of carbonic disulphide, and to this solution a solution of one molecule of bro-

* Ann. Chim. Phys. [3] 67, 139. † Ann. Chem. Pharm. 137, 233. ‡ Ibid. 139, 68.
§ Deutsch. ch. Ges. Ber. 1872, 92. ‖ Bull. Acad. Belgique [2] 33, 1.
¶ J. prkt. Chem. [2] 12, 398. ** Ann. Chem. 188, 51.

†† We propose to call this acid the *αβ*-dibrombutyric acid, from the position of the two bromine atoms towards the carboxyl group. Tollen's dibrompropionic acid would therefore be the *αβ*-acid, and the name *β*-dibromo-acid, which he gave to this acid, would designate the hitherto unobserved third dibromo-acid in which the two bromine atoms are both in the *β*-position towards the carboxyl group. The bromcrotonic from the *αβ*-dibrombutyric acid is designated as the *β*-acid for reasons given below.

mine in the same solvent was gradually added. At first the color of the bromine disappeared rapidly; toward the end of the treatment more slowly. The mixture was allowed to stand twenty-four hours, and the carbonic disulphide then removed by distillation. The acid is easily soluble in alcohol, benzol and ether, and crystallizes from the latter solvent in long, white needles, which melt at 87°. It is but sparingly soluble in cold, more readily in hot water.

The bromine estimation of the pure acid yielded the following result:

		Calculated for $C_4H_6Br_2O_2$.	Found.
Br	...	65.04	65.30

The silver salt could not be obtained in a state of purity, owing to the ease with which it decomposes, with a separation of silver bromide. The yield of the dibrombutyric acid by the method described is almost the theoretical.

The β-monobromcrotonic acid was obtained by treating an alcoholic solution of the above described acid with an alcoholic solution of two molecules of potassium hydrate. When the solutions were mixed a slight increase in the temperature was noticed, and an immediate deposition of potassium bromide took place. The reaction was completed by heating the solution for a few minutes on a water-bath. The potassium bromide was then removed by filtration, the alcoholic solution diluted with eight or ten times its volume of water, made acid with dilute sulphuric acid, and then extracted with ether. Upon evaporation of the ether the monobromcrotonic acid remained as a mass of white crystals; these were recrystallized repeatedly from water until a constant melting point was reached. The analysis of the pure acid gave the following results:

		Calculated for $C_4H_5BrO_2$.	Found.
C	...	29.09	28.75
H	...	3.03	2.87
Br	...	48.48	48.61

The β-monobromcrotonic acid is easily soluble in ether, alcohol and carbonic disulphide, and tolerably soluble in hot water, from which it crystallizes in long, white needles.

The melting point of the pure acid, precipitated from the barium salt by the addition of chlorhydric acid and recrystallized, is 92°.

The silver salt was prepared from an aqueous solution of the ammonium salt by the addition of silver nitrate, and crystallizes in

white needles. It is very stable toward light and quite insoluble in cold water.

		Calculated for $C_4H_4BrO_2Ag$.	Found.
Ag	...	39.66	39.42

The barium salt was obtained by neutralizing an aqueous solution of the acid with barium carbonate; the salt was subsequently crystallized from water. It crystallizes in plates and contains $3\frac{1}{2}$ molecules of water. It is easily soluble in water.

		Calculated for $(C_4H_4BrO_2)_2Ba + 3\frac{1}{2}H_2O$.	Found.
H_2O	...	11.93	11.39

The barium determination in the anhydrous salt gave the following result:

		Calculated for $(C_4H_4BrO_2)_2Ba$.	Found.
Ba	...	29.46	29.51

The calcium salt was obtained in a similar manner to that used for the barium salt. It is easily soluble in water and crystallizes in rhombic plates. The salt contains 3 molecules of water of crystallization.

		Calculated for $(C_4H_4BrO_2)_2Ca + 3H_2O$.	Found.
H_2O	...	12.55	12.69

The calcium determination in the anhydrous salt gave the following result:

		Calculated for $(C_4H_4BrO_2)_2Ca$.	Found.
Ca	...	10.87	10.41

By the action of sodium amalgam the β-monobromcrotonic acid was converted into the sodium salt of an acid which contained no bromine. The acid was separated, purified, and the salts examined. Its properties correspond perfectly with those of the normal butyric acid. The behavior of the calcium salt, and the solubility of the silver salt (1 part of the salt in 24 parts of water) leave no doubt that the acid is normal butyric acid.

The β-monobromcrotonic acid easily takes up one molecule of bromine, forming a tribrombutyric acid.

The monobromcrotonic acid was dissolved in carbonic disulphide and treated with one molecule of bromine also in solution in the same solvent. After standing twenty-four hours the carbonic disulphide was removed by distillation, and there remained a mass of white crystals. These were purified by recrystallization from benzol and analyzed with the following result:

		Calculated for $C_4H_5Br_3O_2$.	Found.
C	...	14.76	15.28
H	...	1.52	1.77
Br	...	73.84	74.07

The tribrombutyric acid is very soluble in alcohol and benzol, and crystallizes from these solvents in large, colorless rhombic plates which melt at 114° without decomposition. It is somewhat soluble in cold water, more freely in hot, but separates from the latter on cooling in the form of an oil which first becomes a solid when a crystal of the substance is brought in contact with it. The acid sublimes much below its melting point. We were unable to obtain salts of the acid in a pure state, owing to the ease with which they decompose, with the formation of a bromide.

If we compare the properties of the above-described bromcrotonic acid with those of Kekulè's brommethacrylic acid, and also of the tribromo-acids obtained from them by the addition of bromine, it will be seen that they are not identical in any respect, and it is therefore evident that Körner's observations were not correct. Furthermore, the reduction of the bromcrotonic acid to normal butyric acid shows conclusively that a molecular transformation has not occurred.

α–Monobromcrotonic Acid.

It became of interest to examine the action of bases on the liquid or α-dibrombutyric acid, and compare the monobromcrotonic acid thus formed with the acid above described. For this purpose a large quantity of dibrombutyric acid was prepared by heating butyric acid with two molecules of bromine in sealed tubes at 130°–140°. Its properties and boiling point corresponded with those given by Friedel and Muchuca.* The acid (one molecule) was dissolved in alcohol and treated with an alcoholic solution of two molecules of potassium hydrate. The action does not take place so easily as in the case of the αβ-acid, and is not completed without several hours heating with reversed condenser upon a water-bath. The potassium salt of the monobromcrotonic acid is easily soluble in alcohol, and the potassium bromide was separated by filtration. The alcoholic filtrate was then diluted with a large volume of water and acidified with dilute sulphuric acid, after which it was extracted with ether. The acid remained as a white crystalline mass, after

*Compt. rend. 54, 220.

the distillation of the ether. It was purified by repeated crystallizations from water and analyzed with the following result:

		Calculated for $C_4H_5BrO_2$.	Found.
C	...	29.09	29.22
H	...	3.03	3.17
Br	...	48.45	48.78

The acid is somewhat soluble in cold water, much more so in hot, from which it crystallizes in long, colorless needles. It is easily soluble in alcohol, ether and benzol, more difficultly soluble in carbonic disulphide. It melts at 106.5°, and is partially decomposed upon boiling. The yield was very small, not exceeding ten per cent. of the amount required by the theory.

The silver salt was precipitated in the form of white needles from a concentrated aqueous solution of the ammonium salt by the addition of silver nitrate. It decomposes slowly in aqueous solution in the cold, with the deposition of silver bromide, very quickly by boiling the solution. The salt is exceedingly sensitive to the influence of light. The analysis gave results as below:

		Calculated for $C_4H_4BrO_2Ag$.	Found.
Ag	...	39.70	40.05

The barium salt was obtained by neutralizing an aqueous solution of the acid with barium carbonate, and was purified by recrystallization from water, in which it is quite soluble. It contains 2 molecules of water, and crystallizes in plates.

	Calculated for $(C_4H_4BrO_2)Ba + 2H_2O$.	Found.
H_2O	7.16	7.11

This monobromcrotonic acid is also obtained by treating the dibrombutyric acid with alcoholic ammonia. We noticed also the formation of the acid, when the α-dibrombutyric acid was heated nearly to its boiling point, fumes of bromhydric acid being given off at the same time.

To examine the action of bromine on the α-monobromcrotonic acid, it was dissolved in a large quantity of carbonic disulphide, and a solution of one molecule of bromine in the same solvent slowly added. After 24 hours the carbonic disulphide was removed by distillation, leaving a mass of white crystals behind. The acid was purified by recrystallization from alcohol, and the bromine estimation resulted as follows:

		Calculated for $C_4H_3O_2Br_3$.	Found.
Br	...	73.84	73.63

The acid separates from water, in which it is easily soluble, in bunches of white needles, which melt at 111°. It is also very soluble in alcohol, ether and carbonic disulphide. We were unable to obtain salts. We do not feel certain regarding the identity of this acid with the acid obtained by the action of bromine upon the β-monobromcrotonic acid. The small quantity at our disposal would not allow a full investigation and comparison, but so far as we are able to judge the acids are *not* identical.

Constitution of α- and β-bromcrotonic Acids.

The rational formula of α-bromcrotonic acid is dependent on that of α-dibrombutyric acid, in which the position of the second bromine atom has not been established, although judging from the action of bromine on other organic acids, the α-position would seem very probable. In this case the bromcrotonic acid obtained from it would have the formula $CH_3—CH = CBr—COOH$. Assuming this probable formula, there remains for the acid from α,β-dibrombutyric acid two possible formulae—$CH_3—CBr = CH—COOH$, and $CH_2 = CH—CBr—COOH$—of which the former is the more probable.

The formation of different bromcrotonic acids from α- and α,β-dibrombutyric acids presents considerable interest, as Tollens has shown that the α- and αβ-dibrompropionic acids yield the same bromacrylic acid. Our results, in thus characterizing an important difference in the properties of substitution products of propionic and butyric acids, indicate that a more thorough and systematic investigation than has hitherto been made of the substitution products of the fatty acids will show further marked differences in the properties of these acids; results which would contribute in no small measure to a better insight into the relations and nature of homologous organic compounds.

Tribrompropionic Acid.

The ease with which bromine adds itself to the above described monobromcrotonic acids indicates the possibility of a like action in the case of monobromacrylic acids, and led us to examine the behavior of bromine towards α-bromacrylic acid, an acid which has been so fully investigated by Tollens. We have modified the methods hitherto in use for the preparation of dibromallyl alcohol in such a manner as to very greatly increase the yield. The allyl

alcohol was dissolved in portions of 20 grams each in 100 grams of carbonic disulphide, and a solution of 60 grams of bromine in 300 grams of carbonic disulphide was allowed to fall, drop by drop, into the solution of allyl alcohol, the latter being kept cool. The bromine is instantly absorbed, and there is a constant tendency to heating, which must be avoided as far as possible. The treatment of a portion of 20 grams should occupy some three to four hours. The carbonic disulphide is then removed by distillation and the dibromallyl alcohol purified by distillation *in vacuo*. The yield of pure dibromallyl alcohol, by this method, rises to 90 per cent. of the amount required by the theory. The dibromallyl alcohol was oxidized according to the method given by Tollens* to dibrompropionic acid and then converted into monobromacrylic acid by treatment with alcoholic potash, separated and purified as recommended by him.† Our observations on all these compounds agree very closely with his. Pure monobromacrylic acid crystallizes in large plates, which melt at 69°.

The process of obtaining the tribrompropionic acid was as follows: the bromacrylic acid was dissolved in a large quantity of carbonic disulphide, and to this solution a solution of one molecule of bromine in disulphide was slowly added. The color of the bromine disappeared rapidly at first, toward the end of the operation more slowly. After standing twenty-four hours the carbonic disulphide was removed by distillation, and there remained behind a very hygroscopic crystalline mass. This was quickly pressed between bibulous paper to remove any traces of carbonic disulphide, then crystallized twice from ether and finally once from benzol, after which the melting point remained constant at 92°. The analysis gave the following results, which correspond with the theoretical figures for tribrompropionic acid:

		Calculated for $C_3H_3Br_3O_2$.	Found.
C	...	11.57	11.50
H	...	.96	1.28
Br	...	77.17	77.25—77.13

The tribrompropionic acid is sparingly soluble in cold water, somewhat more soluble in hot water, from which it separates as an oil which remains liquid as long as it contains a trace of water. A drop of water placed upon the pure acid instantly converts it into

* Ann. der Chemie, 171, 341 (note). † Wagner and Tollens, Ann. loc. cit.

an oil. The acid is not hygroscopic when perfectly pure. It is very easily soluble in alcohol and ether, more difficultly soluble in benzol, from which it crystallizes in beautiful needles. The melting point of the pure compound is 92°, but a small mixture of impurities lowers it in an extraordinary degree. The rational formula is $CH_2Br—CBr_2—COOH$.

We were unable to examine the salts of this acid. The silver salt appears to be exceedingly unstable. The barium and strontium salts are more permanent, but we were unable to obtain them in a state suitable for analysis: they are both very soluble in water. If the tribrompropionic acid is treated with two molecules of potassium hydrate in alcoholic solution, the liquid immediately becomes warm and potassium bromide separates. The solution contains the potassium salt of an acid, which is apparently a dibromacrylic acid.

This tribrompropionic acid does not appear to be identical with the one obtained by Fittig and Petri* by the action of bromhydric acid upon dibromacrylic acid. They found the melting point of their compound to be 53°, while we find the melting point of our tribrompropionic acid to be 92°.

BUFFALO, N. Y., *Jan.* 5, 1880. NATICK, MASS.

ON A NEW SYNTHESIS OF SALIGENIN.

BY WM. H. GREENE.

The method by which I have obtained saligenin synthetically is an application of a general method for the preparation of phenolic derivatives made known by Reimer and Tiemann. Indeed, since by the reaction of chloroform or of carbon tetrachloride on an alkaline solution of sodium phenate, salicylic aldehyde, or salicylic acid may be obtained, it may naturally be expected that, under the same circumstances, methylene chloride would yield saligenin, the latter being an oxybenzylic alcohol.

A mixture of 30 grams of methylene chloride, 30 grams of phenol, and 40 grams of sodium hydrate dissolved in 50 grams of water, was heated in a sealed matrass in a water-bath. The

* Ann. der Chemie, 195, 73.

reaction is complete in about six hours, after which the contents of the matrass are neutralized with hydrochloric acid, and agitated with ether, which takes up the saligenin and the excess of phenol. The ethereal solution is decanted, and the ether distilled off; the residue is repeatedly exhausted with boiling water, which takes up the saligenin, and leaves the greater part of the phenol undissolved. The aqueous solution is concentrated to a small volume, and the drops of phenol which separate on cooling are removed. After exposing the residue for some time over sulphuric acid, a crystalline mass is obtained, which is pressed and recrystallized from boiling water or from alcohol. Pure saligenin is thus obtained.

The quantity of saligenin is by no means in proportion to the quantity of phenol employed, and an alcoholic solution of sodium hydrate yields no better results than an aqueous solution, although the reaction takes place more promptly.

Isomeric oxybenzylic alcohols may be, and probably are, found at the same time, but I have not yet been able to isolate such compounds.

ON THE DECOMPOSITION OF ALCOHOLS, ETC., BY ZINC CHLORIDE AT HIGH TEMPERATURES.

By J. A. Le Bel and Wm. H. Greene.

Wischnegradsky having demonstrated the presence of normal amylene (propyl-ethylene) in commercial amylene, prepared by the action of zinc chloride on ordinary amylic alcohol, we were led to determine whether normal butylene could not be produced by the decomposition of ordinary butylic alcohol by zinc chloride at high temperatures.

Our results induced us to extend the experiment to other alcohols, and the reactions observed, although extremely brutal, are interesting, as they indicate the more stable linkings of the carbon atoms.

The experiments were made in a manner similar to that employed by Etard in the preparation of amylene. The zinc chloride was strongly heated in a mercury bottle provided with two apertures, through one of which the alcohol was allowed to fall upon the fused zinc chloride in a thin stream, or in quick successive drops, while

the other served for the passage of a rather wide delivery tube, so arranged that it could be cleared, if it became obstructed, without discontinuing the operation.

The products of the decomposition were passed through a condensing apparatus and receiver, for the collection of undecomposed alcohol and liquid matters, while the gases were led through bromine, for the absorption of unsaturated hydrocarbons. In some cases a bottle of ammoniacal cuprous chloride was introduced between the receiver and the bromine bulbs, for the retention of acetylene, if present, and the apparatus was otherwise modified to suit the body under experiment. The observations were directed especially to the hydrocarbons formed, and the other products were not examined, except in the cases mentioned.

Methyl Alcohol.

Since the general action of zinc chloride upon the other alcohols results in a dehydration, of which the simple or condensed olefines are the principal products, it was natural to expect that the decomposition of methyl alcohol under the same circumstances would yield analogous results. However, the reaction takes place in an entirely different manner: if the ordinary delivery tube be employed and directly connected with the condenser, the latter soon becomes obstructed by a solid product. A wide adapter was therefore introduced between the mercury bottle and the condenser, and a considerable quantity of a well-crystallized, not very fusible, solid substance sublimed on its sides.

The liquid products contained undecomposed alcohol, water, and a small quantity of non-saturated hydrocarbons, too numerous and in too small quantity for complete investigation.

The gases were washed by passage through sulphuric acid, and then conducted through bromine. The sulphuric acid absorbed a small quantity of methyl oxide, which was subsequently set free by diluting the acid with water. Only traces of gaseous olefines were absorbed by the bromine, the bromides obtained consisting of propylene and butylene bromides. The great mass of the gaseous products consisted of saturated hydrocarbons, of which methane was found to be the principal constituent.

The crystals condensed in the adapter were purified by repeated crystallization from alcohol; they obstinately retain a trace of oily matter, and apparently a volatile product containing chlorine, from

which they cannot well be freed by sublimation. When quite pure they constitute shining white scales, which melt at 160°, and boil at 259–260°. Repeated analysis shows them to be hexamethylbenzol, which was discovered by Friedel and Crafts, by the reaction of methyl chloride on benzol in presence of aluminium chloride. By the courtesy of M. Friedel we were able to compare our product with the hexamethylbenzol obtained by him, and to establish a perfect identity in the crystalline form, and in the picric acid compounds of the substances.

It is not easy to explain the formation of hexamethylbenzol in this reaction. Lest it might be due to the presence of acetone or other impurity in the methyl alcohol employed, the experiment was repeated with absolutely pure methyl alcohol prepared from methyl formate, and kindly furnished us by MM. Bardy and Bordet, who discovered this method for its preparation.* The result was the same as in the first case.

The evolution of small quantities of hydrochloric acid in these reactions was demonstrated. The normal product of the dehydration of methyl alcohol would be CH_2, and it may be easily conceived that acetylene is formed at the same time, and immediately condensed into benzol. We may then consider it possible that methyl chloride may be formed in the presence of benzol and zinc chloride; but the latter acts, in such a case, like aluminium chloride, producing benzol substitution compounds, and the hexamethylbenzol may be formed in this manner. However, it is worthy of note that the most careful experiments failed to indicate the presence of acetylene in the gases evolved.

Ethyl Alcohol. (*Wm. H. Greene.*)

The uncondensed products of this decomposition were passed through petroleum, before entering the bromine bulbs, in order to absorb any butylene which might be formed by polymerisation. Between the mercury bottle and the condenser the vapors were caused to traverse a small bulb containing water, which was afterwards found to have absorbed a small quantity of hydrochloric acid. The unabsorbed gases consisted almost entirely of hydrogen with a trace of ethane.

The bromide obtained was found to be ethylene bromide, containing no higher products, and mere traces of absorbed gases were obtained from the petroleum.

* Comptes rendus, 88, p. 183.

But while thus far the reaction was such as might have been expected, an examination of the condensed liquid showed that in addition to undecomposed alcohol, water, traces of ether, and a small quantity of liquid hydrocarbons, a considerable proportion of aldehyde had been formed. Subsequent experiments demonstrated that the proportion of aldehyde corresponded very closely with that of the ethylene disengaged, and the following equation probably expresses the decomposition:

$$2C_2H_6O = C_2H_4O + C_2H_4 + H_2O + H_2.$$

This may be understood from the following scheme:

$$\begin{array}{r|l} & CH_3 \\ H_2 & COH \\ \hline OH & CH_2 \\ H & CH_2 \end{array}$$

Some paraldehyde is also obtained, and is probably formed by the polymerisation of part of the aldehyde by the hydrochloric acid; the latter is due to the decomposition of the zinc chloride by the water generated, with the formation of oxychloride.

Propyl Alcohol. (*J. A. Le Bel.*)

The decomposition of propyl alcohol is analogous to that of ethyl alcohol; a somewhat larger quantity of oily matter is formed, and perhaps less propionic aldehyde. The chief interest attached to the results lies in the fact that the process is an advantageous one for the preparation of propylene. The unsaturated gaseous hydrocarbons consist almost wholly of that body, and large quantities of propylene bromide may be thus prepared in a short time from propyl alcohol.

Isobutyl Alcohol.

Inasmuch as there was a possibility of the formation of the three isomeric butylenes in this experiment, the gases disengaged were repeatedly washed by passing through sulphuric acid diluted with half its volume of water, in order to remove as much as possible the isobutylene. The absorbing apparatus which we found to answer best consisted of a number of wide, inclined tubes, about half filled with the acid mixture, through which the gas passed rapidly as it was formed. It was then led through bromine, and the bromides obtained were submitted to careful fractionation.

The liquid portion of the product seemed to contain butyl oxide, together with some ethers that were not examined.

About 1500 grams of isobutyl alcohol were employed, and nearly 1000 grams of mixed bromides obtained; the product was divided into three fractions: 145–152°, 152–154°, 154–160°. The latter fraction constituted about three-fifths of the entire quantity, and little or no residue remained at 160°, showing that ethylvinyl, of which the bromide boils at 166°, is not formed in the reaction. The bromide boiling between 154 and 160° consists of the bromide of normal dimethyl-ethylene, but it cannot be completely separated from the lower bromide (isobutylene) by fractional distillation.

The constitution of the bromide (154–160°) was verified by reconverting it into butylene by the action of sodium, again passing the gas through sulphuric acid diluted with half its volume of water, and then into concentrated hydriodic acid. The butyl iodide thus formed was decanted, dried and distilled, and was found to consist entirely of the secondary iodide, boiling at 118–119°: the tertiary iodide boils at 98°.

As we possessed a quantity of the bromide of ethylethylene, boiling at 166°, it was interesting to determine whether, as theory would indicate, the two normal butyl iodides would regenerate the same butylene, or whether the original hydrocarbon would be formed. If each of the hydrogen atoms united to the same carbon atom fill the same function, the hydriodates of normal dimethyl-ethylene and of ethylethylene should be identical—should both be secondary butyl iodide; but if the hydrogen atom be still affected by the iodine atom with which it entered the group, it might be expected that the original hydrocarbon would be regenerated in each case on the removal of HI. The ethylethylene bromide was, therefore, heated with sodium, the resulting butylene was converted into butyl iodide as before, and the iodide was found to boil at 118–121°.

This iodide and that obtained by the preceding operation were separately decomposed by alcoholic potassium hydrate, and the butylenes produced were absorbed by bromine. In each case the bromide obtained was that of normal dimethylethylene, thus showing that the bromide of ethylethylene or ethylvinyl cannot be regenerated.

Normal Butyl Alcohol.

After the preceding experiment, it was interesting to ascertain, by the decomposition of normal butyl alcohol, whether the more stable position of the carbon chain be that of dimethylethylene or of

ethylvinyl. The normal butyl alcohol used was prepared by the fermentation of glycerin by the process of A. Fitz, who furnished one of us with the butyl *bacillus*. The apparatus was arranged as in the preceding experiment, the gases being washed by passing through sulphuric acid, and then conducted into bromine. Immediately at the close of the operation the sulphuric acid was diluted with water at 0°, saturated with sodium hydrate, and distilled. Repeated and careful fractional distillation of the product failed to disclose the presence of trimethylcarbinol, showing that no isobutylene is formed in the decomposition.

Of 138 grams of bromides obtained, 87 grams distilled between 153 and 159°, and only 12 grams passed between 163 and 170°. Naturally, no bromide boiling between 145 and 150° was obtained. Therefore, besides the small quantity of ethylvinyl formed, the only gaseous olefine produced by the reaction consists of normal dimethylethylene, and in this case the normal carbon chain shows no tendency to transformation into a modification having side-chains.

A. Etard * studied the action of zinc chloride at high temperatures upon ordinary amylic alcohol, and considered the product boiling between 35 and 38°, as isopropylethylene, but Wischnegradsky † showed that Etard had obtained trimethylethylene, isopropylethylene boiling at 21.5°.

Aldehyde. (*Wm. H. Greene.*)

The aldehyde was allowed to flow in a thin stream upon the fused zinc chloride, for when dropped, the greater part of it volatilizes immediately on entering the hot mercury bottle.

The gas evolved was passed through ammoniacal cuprous chloride; no acetylenic precipitate was formed. Of the bromides obtained, the greater proportion consisted of ethylene bromide, while a considerable portion of propylene bromide, and a small quantity of higher bromides were obtained.

The condensable products of the decomposition consisted of water, unaltered aldehyde, crotonic aldehyde, and paraldehyde; the latter is attributable to the polymerising action of the hydrochloric acid set free, on the aldehyde which escaped decomposition, a noticeable evolution of hydrochloric acid having been observed in this experiment. As in the other cases, a small proportion of the distillate consisted of a complex mixture of hydrocarbons.

* Comptes rendus, 86, 488. † Ibid. 86, 973.

Acetone. (*Wm. H. Greene.*)

The disengagement of saturated hydrocarbons was comparatively insignificant, and the unsaturated hydrocarbons consisted principally of the higher members of the series; only a small quantity of ethylene bromide, and somewhat more propylene bromide, were obtained, the thermometer then rising rapidly during the fractionation, until it reached 250°, when the distillation was stopped.

It was to be expected that mesitylene would be formed in this reaction, but the quantity of oily distillate was quite small, and no mesitylene could be detected by the most careful examination. However, a considerable proportion of the oily matter which condensed was found to consist of hexamethylbenzol. In order to separate this, the aqueous portion of the distillate was removed, and the lighter layer was distilled until the residue consisted only of the little remaining water and an oily layer. The latter was decanted and again heated until hexamethylbenzol began to sublime; the residue was allowed to cool, strongly pressed, and the hexamethylbenzol was purified by sublimation and crystallization from hot alcohol.

The yield of hexamethylbenzol is very small, not nearly as large as that obtained from methyl alcohol.

Acetic Acid. (*Wm. H. Greene.*)

The gaseous products which escaped absorption by the bromine, consisted of carbon monoxide and carbon dioxide, together with a small quantity of saturated hydrocarbons.

The bromides formed contained a little ethylene bromide, mere traces of propylene bromide, and the bromide of dysymetric dimethylethylene (isobutylene) in considerable quantity. At the same time an appreciable amount of the bromide of normal dimethylethylene was obtained.

The formation of isobutylene in this reaction is quite unexpected, and not entirely intelligible, for a comparison of the relative quantities of the products shows the final results, carbon monoxide, carbon dioxide and butylene, to be in about equal molecular proportions.

ON THE DETERMINATION OF NITROGEN.*

By S. W. Johnson and E. H. Jenkins.

In the Station Report for 1878† the comparative merits of the two methods employed by chemists for the quantitative determination of nitrogen in agricultural products were discussed, and full details were given of the precautions which our experience has led us to adopt in applying the soda-lime process. The notion that the so-called "absolute method" is more exact than the soda-lime process, and that the albuminoid bodies can only be analyzed by the former method, made it necessary to submit both processes to critical experimental study, and our conclusion was that the two methods, when properly worked, give results that agree within 0.05 to 0.15 per cent. We found, moreover, confirmation of the long recognized fact that the errors of the soda-lime process naturally tend to give a deficiency, and those of the absolute method an excess of nitrogen. We give but a brief outline of our mode of working the absolute method. The circumstance that other chemists are still undecided as to the merits of the two processes, and that the absolute method must be frequently employed in the analyses of fertilizers containing both nitrates and organic nitrogen, decides us to give a detailed account of the procedure which we have adopted and which gives us so satisfactory results.

Reagents.

Cupric Oxide.—"Copper scale," which may contain cuprous oxide, coal dust, oil, etc., is mixed in an iron pot with 10 per cent. of potassium chlorate and enough water to make a thin paste. The mass is heated and stirred till dry, the heat is then raised to the point of ignition, and continued until the mass does not glow nor sparkle when stirred.

The potassium chloride is washed out by decantation and the cupric oxide is dried and moderately ignited.

Metallic Copper.—Granular copper oxide, or fine copper gauze, is suitable for its preparation. The granular copper is most con-

* From the Report of the Connecticut Agricultural Experiment Station for 1879. Communicated by the Authors.

† Also this Journal, Vol. 1, p. 74.

venient; copper gauze must be made into rolls adapted to the combustion tube. The copper is reduced and cooled as usual in a stream of hydrogen.

Potassium Chlorate.—Commercial potassium chlorate is fused in porcelain and pulverized.

Sodium Bicarbonate must contain no organic matter.

Solution of Caustic Potash.—Dissolve commercial "stick potash" in less than its weight of water, making a solution so concentrated that, on cooling, it deposits crystals of potassium hydrate.

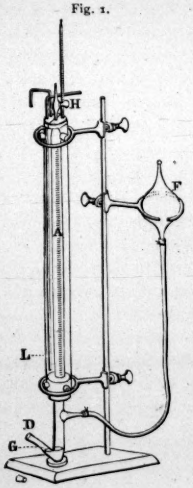
The same clear solution may be used for a number of combustions or until the absorption of carbonic acid gas is not quite prompt.

Apparatus.

The Combustion Tube should be of the best hard Bohemian glass, about 2 feet 4 inches long. The rear end is bent and sealed as in Fig. 3. It is best to protect the horizontal part with thin copper. The tube is connected with the pump by a close-fitting rubber cork, smeared with glycerine.

Azotometer.—This is a modification of the apparatus invented and described by Schiff, *Fres. Zeitschrift*, Bd. 7, p. 430. It is represented in Fig. 1. The gas is measured in an accurately calibrated cylinder (burette), A, of 120 c. c. capacity, graduated to fifths of cubic centimeters, and closed at the upper end by a glass stopcock. The lower end is connected by means of a perforated rubber stopper about 1¾ inches long and 1½ inches diameter, with another tube having two arms, one, D, to receive the delivery tube from the pump, the other connected by a rubber tube with a bulb of 200 c. c. capacity, F, through which potash solution is supplied. The graduated tube is enclosed in a water-jacket with an external diameter of about 1¾ inches. Its lower end is closed by the caoutchouc stopper that connects the two parts of the azotometer described above. The upper end of the jacket is closed by a thin rubber disk slit radially

Fig. 1.

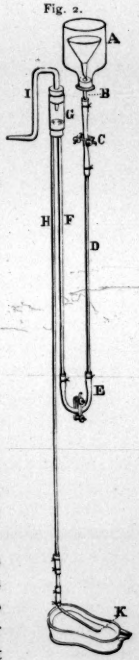


and having four perforations: one in the centre, through which the neck of the graduated tube passes, and three others near the circumference. Through one of the latter, a glass tube, L, bent as in the figure, reaches to the bottom of the jacket, another short tube passes through the disk and the third hole is for supporting a thermometer. The azotometer is held upright and firm on a string by rings fitted around the jacket and by cork wedges.

The bulb for potash solution rests in a slotted, sliding ring.

The air pump used is the Sprengel mercury pump, modified merely so as to be easily constructed and durable. Its essential parts are sketched in Fig. 2. Some of them are exaggerated in order to show their construction more plainly. Through a rubber stopper wired into the nozzle of the mercury reservoir, A, passes a glass tube, B, 4 inches long, this connects by a caoutchouc tube with the straight tube, D, 3 feet long. The rubber tube, E, 6 inches long, connects D with a straight glass tube, F, of about the same length as D.

Fig. 2.



G is a piece of combustion tube 1½ inches long, closed below by a doubly perforated soft rubber stopper admitting the tubes F and H, and above by a singly perforated rubber stopper into which a tube, I, is fitted. The tube H has a length of 45 inches. At the bottom it is connected by rubber with a straight tube of 3 inches, and this again with a tube, K, of 7 inches. The tubes H K should have an internal diameter of 1½ millimeters, F may be 2 millimeters, and D still larger.

We have used for H and F slender Bohemian glass tubes of 4 millimeters exterior diameter. Their elasticity compensates for their slenderness. If heavy barometer tubes be used the stoppers and G must be of correspondingly larger dimensions.

The joints at G must be made with the greatest care.

It is best to insert the lower stopper for half its length into G, having the dimensions of the parts so related that it requires considerable effort to force the slightly greased tubes F and H to their places just through the stopper. The tube I must

be of *stout glass*—a decimeter in diameter. It is drawn out at either end to a long taper, and bent as in the figure, in order to bring its free extremity to the level of the combustion furnace. The hole in the upper rubber stopper has a diameter of 5 mm., just sufficient to admit the narrowed end of the tube, which, after greasing or moistening with glycerine, is "screwed down" into the stopper.

These three joints are the only ones belonging to the pump which have to resist diminished pressure, and require extreme care in making.

If not entirely secure they are to be trapped with glycerine. For this purpose it is needful to pass F and H through a stopper of half an inch greater diameter than G and correspondingly perforated, before entering the latter. Then, previous to inserting I, a tube 4 inches long is slipped over G upon this wider stopper. When I has been inserted and the tubes have been secured to their support, the space between G and the outer tube is filled with the most concentrated glycerine, which is prevented from absorbing moisture by corking above.

The two rubber tubes are both provided with stout screw clamps, to admit of exactly regulating the flow of mercury. The tubes D, F, H, and I are secured to a vertical plank framed below into a heavy horizontal wooden foot on which rests the mercury trough, and having above a horizontal shelf through an aperture of which passes the neck of A.

The tubes D, F, H, and I are secured to the plank at several points by wooden or cork clamps, clasping the tubes and fastened by screws or wires.

These fastenings are made elastic by the intervention of a thick rubber tube between the glass and wood. The connections C and E should be made of stout vulcanized rubber, those at the base of H K of fine black rubber.

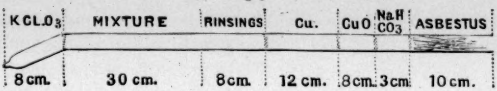
The latter should be soaked in melted tallow previous to use, all excess being carefully removed from the interior. The joints should be wound with waxed silk.

A glass funnel is placed within A to prevent spattering of the mercury when it is filled.

Operation.

From 3 to 4 grs. of potassium chlorate, according to the amount of carbon to be burned, are put into the tail of the combustion tube, Fig. 3, followed by an asbestos plug just at the bend.

Fig. 3.



The substance to be analyzed (0.6–0.8 grams) is well mixed in a mortar with enough cupric oxide that has been *freshly ignited* and allowed to cool, to make a layer 11 or 12 inches long in the tube. The mixture is introduced through a funnel and rinsed with enough cupric oxide to make a layer of 3 inches, a second asbestos plug, and upon it a layer of reduced copper of 4 or 5 inches long are put in, then a third asbestos plug, then 2 inches of cupric oxide, a fourth asbestos plug, then .8 to 1. grams of sodium bicarbonate. The remaining space in the tube is loosely filled with asbestos, to absorb the water which is formed during combustion, and prevent it from flowing back upon the heated glass. The anterior part of the tube containing the cupric oxide and reduced copper is wound with copper foil, leaving, however, a little of the copper (Cu. in fig. 3) visible at its rear. The combustion tube is placed in the furnace at the level of the tube I, and connected with the latter by a close-fitting rubber stopper smeared with glycerine.

Care must be taken to make the joint perfectly tight. The combustion tube has its conical rubber stopper partly inserted, and is then forced and rotated upon the tapering and stout end of the tube I, the latter being supported by one hand applied at the lower bend.

Preparation of the Azotometer.

Fill the bottom of the azotometer to about the level indicated by the dotted line G, with mercury. Close the arm D securely with a rubber stopper. Grease the stopcock H and insert the plug, leaving the cock open.

Pour potash solution into F till A is nearly full, and there is still some solution in the bulb F. Raise the bulb cautiously with one hand, holding the stopcock H in the other hand. When the solution in A has risen *very nearly* to the glass cock, close the latter, avoiding contact of the alkali with the ground glass bearings. Replace the bulb in the ring and lower it as far as may be. If the level of the solution in the azotometer does not fall in 15 or 20 minutes, it is tight. Place the delivery tube of the pump K in a mercury trough.

Supply the vessel A with at least 500 c. c. of mercury. Cautiously open the clamps C and E. If the mercury does not start at once pinch the rubber at E repeatedly. The mercury should flow nearly as fast as it can be discharged at K, without filling the cylinder G. Five to ten minutes working of the pump will generally suffice to make a complete exhaustion of the combustion tube. If most of the mercury runs out before exhaustion is complete, close the clamp C, return the mercury to A, and repeat the operation. When there is a complete exhaustion, the mercury falls with a rattling or clinking sound. After it has been distinctly heard for half a minute, close the clamp C. If the mercury column in H remains stationary for some minutes, the connections are proved to be tight.

Adjusting the Azotometer.

Remove the mercury trough, placing the K in a capsule.

Heat the part of the tube containing sodium bicarbonate. Water vapor and carbon dioxide are evolved, which fill the vacuum in H and expel the mercury. While this is being done place the azotometer near by, remove the bulb F from the ring and support it in a box near the level of D, so that the stopper may be removed from D without greatly changing the level of the mercury G, and so that the azotometer can be moved freely without disturbing it. When the cork in D has been removed fill D half full or more with water.

As soon as the mercury has fully escaped from K insert the latter in D. Let a few bubbles escape through the water, and then pass the tube K down so that the escaping gas enters the azotometer. It will much facilitate the delivery of gas if the extremity of the tube K just touches the inside of the azotometer tube, and is kept, as near as possible, to the surface of the mercury.

The carbon dioxide is absorbed in passing through the caustic potash solution. In spite of all precautions very minute bubbles of permanent gas will occasionally ascend, but, as will be seen on observing the amount of potash solution thus displaced, the error thereby occasioned is extremely small.

The Combustion.

First heat the anterior cupric oxide to full redness, and afterwards the copper. The fine gauze or pulverulent copper very completely reduces any oxides of nitrogen which might be produced

in the combustion, and also retains any excess of oxygen which is evolved at the close of the process.

The anterior cupric oxide burns the traces of hydrogen which may be held by the reduced copper, even when the tube is exhausted, and also destroys the carbon monoxide which is usually formed when steam and carbon dioxide pass together over reduced copper, if iron or carbon be present. Go on with the combustion as usual, bringing the heat up to a fair redness. The flow of gas may be made quite rapid, say one bubble a second, or a little faster.

When the horizontal part of the tube has all been heated, and the evolution of gas has nearly ceased, heat the potassium chlorate so that it boils vigorously from evolution of oxygen. The reoxidization of the reduced copper oxide and of any unburned carbon proceeds rapidly.

When the oxygen, whose flow admits of easy regulation, begins to attack the anterior layer of reduced copper, stop its evolution and lower the flames all along the tube, keeping the reduced copper still faint red.

After a few minutes start the pump, slowly at first, having some vessel under the tube D of the azotometer to receive the mercury. A few minutes pumping suffices to clear the tube. Remove the azotometer, close the tube D with its rubber stopper, then raise the bulb into its ring to such a height that the potash solution in it shall be at about the same level as that in the graduated tube. Connect L at its upper end with a water supply, insert a thermometer in the top of the water-jacket and let the water run until the temperature and the volume of gas are constant.

Read off the volume of gas and the temperature, after having accurately adjusted the level of the solution in the bulb to that in the azotometer.

Read the barometer and make the calculations in the usual way. When 50 per cent. potash solution is used, no correction need be made for tension of aqueous vapor, as Schiff has shown.

The calculation is somewhat shortened by the use of the table in *Jour. of Chem. Soc.* Vol. 18 (1865), p. 212.

Very fair results are got by employing, with suitable precaution, a stream of carbon dioxide to displace the air of the combustion tube, but the process is very tedious, the sources of error are more numerous, and the results are apt to be higher and not so accordant as when the mercury pump is used to evacuate the tube.

The pump above described has been in use for eighteen months without any repairs, and by its help two or even three analyses may be performed in a day.

The paper in Station Report for 1878, already referred to, gives results of analyses of a variety of substances by the method above described.

Some additional comparative analyses recently made by Dr. Jenkins, on carefully prepared, but not dry, albuminoids have given the subjoined results for nitrogen:

	By Soda Lime.	By Absolute Method.	Average Differences.
Albuminoid of Pea Nuts, - -	15.95	15.92	——
Legumin of Peas, - - -	15.32–15.27	15.41	0.11
Conglutin of Almonds, - - -	16.32–16.37	16.59	0.25

GUM LAC FROM ARIZONA.

By J. M. Stillman.

There was received lately at this University, sent by Mr. John A. Culbertson, of Phœnix, Arizona, a quantity of a substance of resinous character, forming a coating of considerable thickness on the twigs of a plant called in that neighborhood "Greasewood," but which I am assured by Prof. Hilgard and by Dr. A. Kellogg is the *Larrea Mexicana*. The plant was identified by means of leaf, flower and seed sent by Mr. Culbertson. The specimens were gathered in the vicinity of that place on the 22d of December last.

The form of occurrence is precisely the same as that in which the gum lac of India is said to occur, as a coating of hard, brittle resin of a reddish color. The gum lac from Siam is said to occur sometimes in deposits of a quarter of an inch in thickness. None of these specimens are so thick, but some exceed ⅛ inch in thickness, and most are of nearly that thickness.

The gum lac of India is of cellular structure, and in these cells are developed the ova of the insect (*Coccus lacca* or *C. ficus*) whose puncture is said to cause the exudation. These cellular cavities contain at the proper season a red substance, which probably serves as the food of the young insects and in which the eggs are deposited.

The specimens from Arizona exhibit the same structure, and in working with the gum the fingers were frequently stained by the crushing of the pulpy substance of blood-red color, in which the eggs could be readily perceived with the lens or microscope.

The following characteristic properties of the gum lac, given by various authors, have been found to be also properties of the specimens examined by me.

(1) Contains a red coloring matter, partly soluble in water (and resembling cochineal). I found 3 per cent. of such coloring matter by one method, 1.4 per cent. by another method given below. (2) Partly soluble in alcohol with a reddish color. (3) Almost entirely soluble in dilute caustic alkalies with a deep red color. (4) The resin of the gum lac (shell lac) is soluble in dilute borax solutions on heating with a purplish red color, and the solution has a peculiar sweetish odor. The resin of this product also is soluble in dilute borax solution, the color is a little brighter red and the odor a little stronger than in the case of the shell lac, but this may be owing to the greater freshness of the Arizona product, as the shell lac used for comparison was at least four or five years old. (5) The lac resin softens at comparatively low temperatures. This product becomes soft and plastic when it feels but just warm to the touch. (6) When warm has a peculiar aromatic odor.

Quantitative analyses of the crude lac (stick lac) have been made by different chemists with varying results.

Hatchett.		Dr. John.		Franke.	
Resin	68.0	Resin sol. in ether	66.65	Resin ..	65.7
Wax	6.0	" insol. "	16.75	Substance of the lac	28.3
Coloring matter	10.0	Coloring matter ..	3.75	Coloring matter	0.6
Gluten	5.5	Extractive ..	3.92		94.6
Foreign bodies ..	6.5	Insect skins ..	2.08		
Loss	4.0	Wax	1.67		
		Laccic acid ..	0.62		
		Salts	1.04		
		Sand	0.62		
		Loss	2.90		

It will be seen from these that *exact* analysis of the lac into its various constituents could not identify it with the India lac when no two analyses agree on the constituents nor on the proportions, the resins being given at from 65.7 to 83.40, and coloring matter at from 0.6 to 10.0 per cent. A partial analysis, however, was made for the purpose of establishing identity as far as could be done by this means.

A portion of the Arizona stick lac was carefully removed from the twigs and boiled with water, and in this way 3.0 per cent. of deep red coloring matter (colored extract) was obtained. The residue was extracted with boiling alcohol, and about 61.7 per cent. of alcoholic extract, probably mostly resin. Of the residue the greater portion was soluble in dilute caustic potash with deep red color, and reprecipitated by acetic acid for the most part, though a certain coloring substance soluble in caustic potash, but not precipitated by acetic acid, could be detected by again neutralizing the acid filtrate.

A second more thorough examination was made by first extracting the powdered resin, dried before weighing, with hot absolute alcohol, which was found to leave the coloring matter nearly all behind; then extracting the residue with boiling water, and extracting the residue from this with dilute caustic potash. The final insoluble residue was dried and weighed, the alcoholic extract and deep red aqueous extract both evaporated, dried and weighed, and caustic potash solution precipitated with acetic acid, filtered, washed on the filter, and the precipitate dried and weighed. By this process there was lost a certain amount of coloring matter insoluble in water but soluble in caustic potash, but not precipitated by acetic acid, but easily detected in the filtrate and wash-water.

The results of these determinations gave—

Resins, &c., soluble in absolute alcohol, . .	61.7
Coloring matter, (soluble in water) . . .	1.4
Caustic potash extract, ("lac stuff"?) . . .	26.3
Insoluble residue, ...	6.0
Loss, (including some coloring matter) . .	4.6
	100.0

The 26.3 per cent. seems to correspond to what Franke calls "material of the lac" (Muspratt), of which he finds 28.3 per cent. in India stick lac.

It will be seen then how closely the gum lac from Arizona agrees in characteristic properties, structure and chemical composition with the India varieties. The differences in the analyses quoted are due doubtless partly to different methods of analysis, partly to real differences in different specimens (this is probably peculiarly applicable to the coloring matter), and partly to different interpretations of the results of analysis.

I am informed by Mr. Culbertson that the insect and gum are also found on a thorny bush called "cat-claw" by the residents. It would be very interesting to have the insect identified or compared with the Indian coccus, as their mode of life as well as the products of their activity appear identical.

Since writing the above communication I have received from Arizona specimens of the lac coating the twigs of that plant which is identified by Professor Hilgard, of this University, as the *Acacia greggii.*

The lac from this source agrees in its main chemical properties with that from the Larrea, behaves the same towards the reagents mentioned in the previous description. It resembles it also in general appearance and in its irregular cellular structure.

It is however much scantier on the twigs of the Acacia, and the amount of coloring matter is notably less. This is shown by the color of the caustic potash solution, and of the borax solution being much lighter red than the solutions of the lac from the Larrea, and also by the fact that the specimens of Acacia lac examined gave no red coloration to water by boiling. It was noticed, however, that when alkalies were added to this water, the color became a bright red. A quite appreciable quantity of alkali was needed before this action took place, pointing to the existence of an acid in the lac which had first to be neutralized before the color could be reddened—possibly Dr. John's *laccic acid* (Muspratt's Chemistry). It is quite possible that this difference in contents in coloring matter is simply due to the fact that the two specimens represented different stages of development. The twigs of the Acacia were dry, and the leaves fallen when these specimens were collected. No fresh insect eggs with the purple juice, with which they are covered, could be detected in the cells of these specimens, while in the specimens from the Larrea this was frequently observed, and moreover the Larrea was in leaf and flower when the specimens were collected. It is quite possible that at other times this difference in the amount of dye-stuff may not exist.

From observations by a number of gentlemen acquainted with that portion of the country, it appears that the Larrea lac is very widely distributed throughout Arizona and the southern part of California (Mohavo and Colorado deserts), and the gum is used by the inhabitants in place of solder for mending kettles, etc. This

use is suggestive of the use of the India lac for the manufacture of sealing-wax. Experience must show whether these products are of such quality as to eventually prove of commercial value.

UNIVERSITY OF CALIFORNIA, *March* 11, 1880.

ETHEREAL OIL OF CALIFORNIA BAY TREE.

BY J. M. STILLMAN.

The California bay tree, known under the different botanical names of *Oreodaphne Californica*, *Laurus Californica*, *Tetranthera*, and latterly *Umbellaria Californica*, is a large and beautiful evergreen tree, very common to the valleys and water-courses of the coast mountains of California. It often attains great size, and its timber is much used under the name of "California laurel" for veneering and fine cabinet-work. The leaf is in shape something like the laurel, but lighter in color and narrower. Both leaf and wood have a very fragrant aromatic odor, which when strong, as in the crushed leaf, excites the mucous surfaces, brings tears to the eyes and produces headache.

The oil was obtained by distilling the leaves (which were gathered in March 1879 when the trees were in bloom) with steam. In the neighborhood of sixty or seventy pounds of the fresh leaves were placed in a large barrel with perforated false bottom, and steam from the escape-pipe of a steam-boiler forced through the mass and condensed. In order to avoid the accumulation of too large an amount of water, this was siphoned off from the bottom of the receiving bottle, the siphon dipping into a dish of water by the side of the bottle, and the overflow of this dish kept the water in the bottle at a constant level. At the end of two days there were obtained in this way 820 grams of the oil. The oil as thus obtained is of a clear yellowish or straw color, of the peculiar aromatic odor of the leaf, specific gravity at 11° C. 0.94. By long standing (nearly a year) it does not thicken.

Subjected to fractional distillation it gives up a small quantity of dissolved water, and separates into two principal fractions, one boiling from 170–190° C. and the other from 210–225°, with smaller quantities passing over as high as 260°.

The lower fraction mentioned was subjected to repeated fractional distillation, and gave a considerable quantity of a clear, colorless, mobile liquid boiling at 167–168°, though apparently with slight dissociation, as traces of water appeared in the first portions of the distillate at each distillation, which were not to be got rid off by repeated distillation and removing the first portions of each distillate. A portion of the purest of this substance from 167–168° C. was subjected to elementary analysis.

	I.	II.	Mean.	Calculated for $C_{20}H_{32}.H_2O$.
C ...	82.91	82.46	82.68	82.76
H ...	11.93	11.68	11.80	11.72

It will be seen that the agreement is very close with the composition of a hydrate of turpentine in which one molecule of water is combined with two of $C_{10}H_{16}$ or one of $C_{20}H_{32}$.

This agrees with the terpinol of Wiggers, investigated and named by List, and obtained in various ways from the turpentine dihydrate $C_{10}H_{16}.2H_2O$. The boiling point of terpinol is given at 168°, and it is a colorless liquid of pleasant aromatic odor. The odor of the compound analyzed is not unlike that of spirits of camphor, though not quite identical.

It is not readily affected by metallic sodium, even when heated with it. The water is therefore in intimate combination, possibly as an ether $(C_{10}H_{17})_2O$.

A vapor density determination was made by Mr. J. B. Wilcutt according to Victor Meyer's method, in diphenylamine vapor. The result in one case gave 4.7, whereas the vapor density calculated for $C_{20}H_{34}O$ would give 10.0. If, however, dissociation should take place, splitting up the molecule into $C_{20}H_{32} + H_2O$, the vapor density of the mixture would be 5.0, not so far from the result obtained. That dissociation would take place was to be foreseen from the behavior on distillation, and was confirmed by the fact that after the operation the contents of the apparatus no longer had the original camphor-like odor, but possessed a distinct, rank odor of turpentine. It was also noticed that the compound itself by long standing bleached the cork of the test-tube, probably due to traces of the free $C_{20}H_{32}$ resulting from the distillation.

An analysis was made of a fraction boiling at 171–172°, which gave C=81.39; H=11.40. Evidently therefore a mixture of the above with the more oxygenated, higher-boiling constituent, umbellol, $C_8H_{12}O$.

The higher fraction (210–225°) was also subjected to fractional distillation and a compound obtained in considerable quantity boiling without decomposition at 215–216° (uncorrected). This substance is also a colorless mobile liquid of aromatic but powerful odor which, too strongly inhaled, attacks the mucous surfaces and causes headache. It is but slightly volatile, a quantity in an open watch-glass losing one mg. in an hour and a half. With concentrated sulphuric acid it gives a blood-red color, turning to brown and black. Water separates it from its solution in the acid. It is acted on violently by sodium, forming a blood-red, brittle, resinous substance; it is also acted on violently and decomposed by strong nitric acid. Elementary analysis gave

		I.	II.	III.	Calculated for $C_8H_{12}O$.
C	...	77.28	77.27	77.17	77.42
H	...	9.74	9.53	9.57	9.67

The vapor density determined, with the assistance of Mr. F. Slate, according to Victor Meyer, in diphenylamine vapor gave 4.39; calculated for $C_8H_{12}O = 4.29$. The formula is therefore $C_8H_{12}O$.

It is isomeric, as far as I know, with no other known compound. It is homologous as far as its empirical formula is concerned with common camphor, but has different properties.

Analysis III. above was made two or three months later than the other two, after the substance had been standing in a test-tube corked, with occasional removal of the cork. It will be noticed that oxidation is very slow if it takes place at all, though a faint tint of yellow seemed to indicate such action. Experiments have been commenced with the object of determining the nature of these substances and their chemical constitution if possible, and I intend to subject the reactions and derivatives of these interesting compounds to an extended investigation. As other duties, however, entirely occupy me at present, I have been compelled to postpone further investigation on this subject for some months. I therefore make this preliminary report and take the opportunity to reserve the ground for future work.

Univ. of California, *Feb.* 1880.

THE ELECTROLYTIC METHOD AS APPLIED TO CADMIUM.

By Edgar F. Smith.

Electrolytic Estimation of Cadmium.

During the past few months I have made additional experiments upon the electrolytic estimation of cadmium, and as they perhaps may be of some interest, I give them here.

1. 0.1209 gram cadmium oxide was dissolved in dilute hydrochloric acid, and to this solution an excess of pure sodium acetate added. I diluted with water to 25 c. c., and then connected the platinum crucible containing the mixture with the zinc pole of a two-celled bichromate battery. At the end of three hours the metal was completely precipitated in a regular, crystalline mass on the crucible sides. After washing with water, alcohol and ether, the crucible was dried and weighed. The cadmium found was 0.1049 gram; the CdO taken requires 0.1057 gram Cd.

2. 0.1087 gram CdO treated as above yielded 0.0950 gram Cd. Required Cd = 0.0951 gram. Time necessary for precipitation about the same as in 1.

3. In this experiment 0.1003 gram cadmium oxide was dissolved in an excess of nitric acid, and to this were added 3 c. c. of concentrated sodium acetate solution, and the whole then diluted to 25 c. c. with distilled water. In four hours the precipitation was complete. The deposit was not, however, as light colored as in case of the chloride. The salt can nevertheless be used, and where cadmium has been precipitated as sulphide it is only necessary to dissolve the same in as little acid as possible and add an excess of sodium acetate solution. The amount of cadmium found in the above example was 0.0877 gram, while the required amount was 0.0880 gram.

4. Dissolving 0.0832 gram cadmium oxide in dilute sulphuric acid I added as in previous experiments an excess of an alkaline acetate, and allowed the electric current to act upon the diluted solution for several hours. The deposition of the metal was rapid and in a beautiful, regular form. The oxide taken required 0.0728 gram metal, and I obtained 0.0725 gram.

5. Treating 0.1098 gram CdO as just mentioned, I found 0.0955 gram Cd instead of 0.0960 gram.

6. Again 0.1039 gram CdO yielded 0.0907 gram Cd instead of 0.0909 gram.

The appearance of the cadmium and the rapidity with which it separated from a sulphate solution containing an alkaline acetate led me to experiment with a pure sulphate solution. According to Wrightson,* this salt is little adapted to the electrolytic estimation of cadmium. My results, however, indicate just the opposite. In my first experiment I used a neutral sulphate solution.

1. 0.1110 gram CdO in form of sulphate was dissolved in 25 c. c. water and the usual battery connection adjusted. In two hours I obtained 0.0968 gram Cd instead of 0.0971 gram. Deposit regular and crystalline.

The next thing to be ascertained was whether the presence of free sulphuric acid was disadvantageous or not.

2. 0.1085 gram CdO was dissolved in sulphuric acid. 2 c. c. free H_2SO_4 (1.095 sp. gr.) were present. Diluted with water to 25 c. c., and in two hours the precipitation of the metal was finished. Found 0.0931 gram Cd instead of 0.0949 gram.

3. 0.1502 gram CdO in form of sulphate, with 2 c. c. H_2SO_4 (1.095 sp. gr.), and diluted with water to 27 c. c., yielded in three hours 0.1327 gram Cd instead of 0.1314 gram.

4. 0.1125 gram CdO as sulphate, having the same amount of free acid present, and being diluted to 25 c. c., gave in two hours 0.0986 gram Cd. Required Cd = 0.0984 gram.

5. 0.0897 gram CdO yielded 0.0863 gram metallic cadmium instead of 0.0860 gram.

The slight increase noticed in these examples is due to impurities in the salt employed. I prefer the sulphate to any other salt for the electrolytic estimation of this metal. When larger quantities of substance are taken than above given, it is advisable to place the cadmium solution in a beaker-glass and in this to suspend a crucible, upon which the deposit of metal may occur.

Separation of Copper from Cadmium.

In solutions of cadmium containing free nitric acid the electric current does not throw down the metal. Copper under the same conditions, however, is precipitated, providing too large an excess

* Zeitschrift anal. Chemie, 15, 303.

of acid is avoided. In accordance with these facts I made several experiments with a view of separating the metals in this manner. These and their results are as follows:

Taking a mixture composed of 0.2220 gram copper sulphate and 0.0762 gram cadmium oxide in a little dilute nitric acid, I added to the same 2.5 c. c. concentrated nitric acid, then diluted the same with distilled water to 75 c. c. In this solution, contained in a beaker, I suspended a weighed platinum crucible connected with the zinc pole of a two-celled bichromate battery. A platinum wire dipping into the solution was attached to the opposite pole. In the course of six hours I carefully removed the crucible, upon which there was a fine copper coating, from the solution, taking care, however, not to interrupt the current until the vessel was entirely out of the acid liquid. The copper deposit was washed with water and alcohol, then dried and weighed. The amount of copper found was 0.0562 gram, the calculated 0.0564 gram. The deposit was dissolved and examined for cadmium, but none found. Nor was there any copper remaining in the cadmium solution. The amount of cadmium was not estimated in this instance, as some of the solution was lost by accident.

In a second experiment I took 0.3435 gram copper sulphate and .0911 gram CdO. These were dissolved in 100 c. c. water containing 3 c. c. concentrated nitric acid. The same battery power as already mentioned was employed. Allowing the current to act during the night, I obtained on the following morning 0.0874 gram Cu instead of 0.0873 gram calculated. This proved to be perfectly free from cadmium. The liquid containing the cadmium solution was evaporated to 50 c. c., potassium hydrate added in excess, and then a potassium cyanide solution sufficient to redissolve the precipitated cadmium hydrate. The crucible was again suspended in the liquid, and in five hours the cadmium was precipitated in fine, regular form. Four bichromate cells were employed. The found cadmium equalled 0.0789 gram instead of 0.0797 gram calculated.

Again in a third experiment I took 0.3070 gram copper sulphate and 0.0787 gram cadmium oxide. The solution was of the same dilution as before, containing also the same quantity of free acid. The deposited copper weighed 0.0779 gram and the calculated 0.0780 gram. No cadmium was detected in it. The cadmium thrown out by the current from a cyanide solution was 0.0690 gram instead of 0.0688 gram. Copper was not discovered in the

cadmium solution. Instead of employing a cyanide solution for the precipitation of the cadmium, the nitric acid solution can be evaporated with sulphuric acid after the removal of the copper. The results with a sulphate solution are just as accurate.

LABORATORY OF THE UNIV. OF PA., *March* 15, 1880.

GALLIUM IN AMERICAN BLENDES.

BY H. B. CORNWALL.

Having observed the spectrum of the principal line of gallium, wave-length 417, I treated two European blendes and several American ones as follows. About one gram of each was treated with aqua regia, the solutions saturated with hydrosulphuric acid, filtered, evaporated to dryness, the residues redissolved in water containing a little hydrochloric acid, and the solutions treated with sodium carbonate until a slight precipitate formed. According to Lecoq de Boisbaudran these precipitates contained the greater part of the gallium which might be present. Each precipitate was dissolved in hydrochloric acid, evaporated nearly to dryness, redissolved in a few drops of water and observed with a single prism spectroscope and an induction spark from a coil capable of giving a five centimeter spark, but worked with a battery developing only about two-fifths of the power of the coil. Separate electrodes and glass tubes were used for each blende.

One European blende, from Pierrefitte, of medium richness according to de Boisbaudran, showed scarcely a trace of the gallium line; the other European specimen, from Santander, classed among the richest in gallium, showed it distinctly. The compact, greyish blende from Friedensville, Pa., showed it about as plainly, while a crystallized, rather dark, yellowish-brown specimen from Phœnixville, Pa., showed it more distinctly still. Two measurements of its position were made with a cross-hair eye-piece and vernier scale. They gave 416.92 and 417.05, mean 416.98.

To test the comparative richness of these blendes, two grams of each were treated with aqua regia, the solutions saturated with hydrosulphuric acid, filtered, evaporated to dryness, redissolved

in water containing a little hydrochloric acid, and each solution diluted to five cubic centimeters. The Phœnixville blende showed the gallium line distinctly enough for approximate measurement. Two determinations gave 417.20 and 417.28. None of the other blendes responded to this test.

Finally, the gallium line was seen in a solution of about one gram of the Phœnixville blende, which had been prepared simply by treatment with aqua regia, filtration from undissolved sulphur, and concentration to a few drops.

The following minerals were also examined by the first method detailed above, viz.: zinc blende from Joplin, Mo.; Ellenville, N. Y.; Roxbury, Conn.; Warren, N. H.; Mine Hill, N. J.; calamine from Friedensville, Pa., and Sterling, N. J.; willemite, zincite and franklinite, from Franklin, N. J.

There is reason to believe that gallium occurs in the blendes from Joplin, Warren and Ellenville, since its line was seen more or less distinctly in case of each, and although the same electrodes were here used for all which had been previously used with a slightly stronger gallium solution, yet they were boiled with hydrochloric acid before each observation. Moreover, no gallium was detected in the case of the other three blendes and all of the oxidized minerals, the observations on which were irregularly interspersed among the others. Gallium may occur among blendes as rubidium does with the alkalies, widely spread in very small quantities.

Examination of other American zinc ores and products is still in progress, according to the simple and severe test applied to the Phœnixville blende, to ascertain whether any richer source of gallium exists here.

JOHN C. GREEN SCHOOL OF SCIENCE, PRINCETON COLL., *March* 5, 1880.

NITRIFICATION IN STANDARD AMMONIUM CHLORIDE SOLUTIONS.

BY H. B. CORNWALL.

The experiments of Warrington* on nitrification induced in dilute ammonium chloride solutions, containing acid phosphate of potas-

*Chem. News, Dec. 14, 1877.

sium and seeded with surface soil, led him to the conclusion that darkness was apparently essential to the operation.

In the *Am. Jour. Sci.*, June, 1878, Storer gives several results which seem to support this view, so that Leeds* was induced to examine a standard solution of ammonium chloride, and stated that his experiments "confirm these results, so far as the change of the ammonium solutions in the dark is concerned, and give the rate at which it may be expected to occur under ordinary circumstances."

As long ago, however, as Nov. 26, 1877, Schloesing and Müntz† had stated that, in certain of their experiments, nitrification went on as well in the light as in the dark; a result similar to that obtained by E. W. Davy.‡

As I had been constantly making up my dilute ammonium chloride solution, for the "ammonia process" in water analysis, from a stronger standard solution of 3.15 grs. fibrous, commercial ammonium chloride in 1 litre of water, which had already stood nearly the whole of four years in a dark place, it became an object to ascertain whether any important change had taken place in it. Accordingly, in April, 1879, I made three determinations of the ammonia, precipitating as ammonio-platinic chloride and weighing the platinum after ignition, using 100 c. c. for one determination and 50 c. c. for each of the others.

Leeds had found that his standard solution, made with 0.7867 gr. of ammonium chloride to the litre, yielded only 0.00023 gr. of ammonia per cubic centimeter, instead of the 0.00025 which it should have given. Reduced to figures directly comparable I found in my three determinations 0.0002461, 0.0002461 and 0.0002465 grs. This solution therefore had lost less than one-sixtieth of its ammonia, instead of nearly one-twelfth, which Leeds found in a solution but one year old, and was consequently not practically injured for use in the water analysis.

The strength of my solution may have had some influence, but Storer's solution was equally strong, yet he reports a strong reaction for nitrites after about a year. As Leeds states that his solution showed a filamentous, apparently vegetable growth, while mine showed only a slight scaly deposit, probably from the glass of the bottle, it may be that the changes in some cases are due to the accidental introduction of germs from the atmosphere.

* Proceed. Am. Chem. Soc. Vol. 2, Dec. 5, 1878. † Comptes rendus, 85, 22.
‡ Chem. News, Dec. 3, 1879.

LABORATORY NOTES.

By Wm. L. Dudley.

On a Modification of Böttger's Test for Sugar.

The importance of an expeditious and reliable test for sugar is well understood, and in many cases where the presence or absence of sugar is of vital importance it is well to employ several tests in order to verify the results; and with this end in view I have been conducting some experiments with the bismuth test.

Böttger's test, which employs subnitrate of bismuth and sodium carbonate or sodium hydrate, is a good one; but the subnitrate is liable to contain silver, which on exposure to the light will give it a gray color. Also other impurities, having a tendency to render the results more or less unreliable, are often present.

After considerable experimenting the following modification was found to be very reliable: Dissolve subnitrate of bismuth in the least possible quantity of chemically pure nitric acid, and add to it an equal amount of acetic acid of ordinary strength; dilute to 8 or 10 times its volume, and filter if necessary. To the solution to be tested add sufficient sodium hydrate to render it strongly alkaline, then add a drop or two of the bismuth solution; heat to boiling and continue the boiling for a short time (20 to 30 seconds). If sugar is present, the white flocculent precipitate which formed on the addition of the bismuth solution to the alkaline liquid will become gray or black. The depth of color of the precipitate depends on the amount of sugar present. If the amount of sugar be very small the gray or black precipitate forms slowly, and it is necessary to allow it to stand for some time (10 or 15 minutes). This reduction occurs in the cold after standing quietly for 24 to 48 hours.

The bismuth solution will remain unaltered, and can be diluted to any degree without the precipitation of the bismuth.

In comparative tests with solutions of glucose, this test proved quite as delicate as Fehling's or Trommer's copper tests, and it undoubtedly can be used in many cases with great advantage, especially in conjunction with the above well-known tests. If albumen is present it must be removed before applying the test for sugar.

A New Test for Gallic Acid.

Prepare a solution of ammonium picrate by adding to a dilute aqueous solution of picric acid, an excess of ammonium hydrate. Add a few drops of this reagent to an aqueous solution of gallic acid, and there is produced, at first, a red color, which in a few seconds becomes a beautiful green; the depth of color depending on the amount of gallic acid present.

Pyrogallic and tannic acids produce, at first, a reddish color, but there is no further material change.

Miami Medical College of Cincinnati, O., *March* 22, 1880.

DETECTION OF HYDROCHLORIC ACID BY SULPHURIC ACID AND ACID POTASSIUM SULPHATE.

By H. W. Wiley.

This well-known test is more conveniently made in the following way than by distillation in a retort as recommended by Fresenius and others. Two small beakers are used, the smaller of which will fit into the larger, leaving a space of two or three centimetres between the two bottoms. The chloride and chromate are well rubbed together and placed in the larger beaker, care being taken that none of the particles adheres to the side of the vessel.

A few drops of sulphuric acid are added, and the smaller beaker put in place. A lump of ice, and if necessary a little salt, is then placed in the smaller beaker.

The chlorochromic acid (so called) is given off at a very gentle heat and is readily condensed on the cold surface of the small beaker. If there is more than a mere trace of chloride a watch glass can be substituted for the inner beaker. After the reaction has ceased the small beaker is removed, and the usual test (ammonium hydrate) is applied.

I extend and modify this test in the following ways:

1. After adding a drop of ammonia to the chromium oxychloride (still on the bottom of inverted beaker) acetic acid is added in excess. A drop of lead acetate is then added. Lead chromate is precipitated. This will detect hydrochloric acid when so little is present that the change of color with ammonia is not perceptible.

2. This is an easier and far more delicate reaction. In fact it seems quite as delicate and far more striking than the test with silver nitrate. The chromium oxychloride is prepared as above. With a stirring rod a fraction of a drop of sulphuric acid is placed in a porcelain dish, and by its side a minute crystal of strychnia. The stirring rod is then touched with the oxychloride, and this is stirred with the sulphuric acid and strychnia. The "color test" for strychnia is developed with even greater brilliancy than with potassium pyrochromate. The merest trace of a chloride is most unmistakably revealed by this test.

If bromides are present they do not at all interfere with the above reaction. Bromine itself with strychnia and sulphuric acid will not give the color test. If bromides are present, moreover, it is not difficult to detect them at the same time with the chlorides. The bromine formed is readily condensed and can be then easily detected. With iodides the case is quite different. In many cases I have found no trace of chromium oxychloride when both chlorides and iodides are present. At other times, the iodine which is set free seems to be dissolved in the oxychloride. In such cases on adding ammonia to the reddish yellow liquid, the whole mass turns black from the formation of iodide of nitrogen. On filtering this off the reactions for the chloride can be obtained in the filtrate, but without exactness. The iodide of nitrogen on the filter paper will, when dried, explode spontaneously, or when scratched or jarred. Prepared in this way the iodide of nitrogen appears to be of a better quality than that prepared by the ordinary methods.

I have yet to investigate the order of succession of the phenomena above mentioned as influenced by varying proportions of the several substances in the mixture. I have not been without a suspicion that bromides might possibly give rise to a trace of chromium oxybromide when treated as described. I have not, however, been able to procure an absolutely pure bromide with which I could subject the matter to the test of experiment. All the authorities, however, which I have consulted, agree that only pure bromine is produced. The bromides I have tried have all given faint reactions by the strychnia test, but I cannot say that they do not contain a trace of chlorine. If some one in possession of an absolutely pure bromide would make the experiment the result would be of interest. I am still investigating the anomalies produced by the admixture of iodides.

LAFAYETTE, INDIANA.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

V.—EXPERIMENTS IN THE PARA SERIES.

By Ira Remsen and Lyman B. Hall.

In the second paper of this series a substance was mentioned* incidentally which was obtained from coal-tar xylene as a secondary product in the preparation of the sulphamides. This was examined to a sufficient extent to warrant the conclusion that it is a derivative of paraxylene. It was converted by simple reactions into paratoluic and terephthalic acids, so that there could be little doubt in regard to its nature. It was also subjected to oxidation and thus converted into a monobasic acid, sulphamineparatoluic acid, the structure of which, however, was not determined by experiments. The belief was expressed that in the acid the sulphamide group would be found to be in the meta position with reference to the carboxyl, and in the ortho position with reference to the methyl. The question as to the structure of the acid has now been satisfactorily answered and the prediction shown to be correct. The details of the investigation are herewith communicated.†

Oxidation of Paraxylenesulphamide.

The sulphamide of paraxylene, separated from the mixture obtained from commercial xylene, was treated with the ordinary chromic acid oxidizing mixture, the proportions used being these:—

7.5 grams amide, 20 grams potassium pyrochromate, and 30 grams concentrated sulphuric acid diluted with three times its own volume of water. This mixture was heated gently for several hours, six to eight being usually sufficient. On cooling, a crystallized mass separates and increases in quantity for some time. This is now filtered off and washed with cold water, until the wash-water passes through uncolored. In order to separate the new acid from any amide which may have escaped the action of the oxidizing mixture, the whole mass is dissolved in dilute sodium carbonate and the solution evaporated down to a small volume.

* This Journal, 1, 137.

† The experiments, as far as paraxylene itself is concerned, were performed by Dr. M. W. Iles.

On cooling, the amide crystallizes out. After separating the amide, the acid is precipitated by the addition of hydrochloric acid. The precipitated acid is again filtered and washed, and now recrystallized from water. It is thus obtained in the form of crystals, which have every appearance of purity. It fuses instantly at 267° (uncorrected).

The method of formation of the acid, taken together with the analyses of its salts communicated below, shows clearly that it is sulphamineparatoluic acid.

Sulphamineparatoluic acid, $C_6H_3\begin{cases}CH_3(1)\\SO_2NH_2(2)\\CO_2H(4)\end{cases}$, is very difficultly soluble in cold water, comparatively easily in hot. It crystallizes from an aqueous solution in beautiful large crystals of a silken lustre, which fuse at 267° (uncorrected) and 274° (corrected). It is very readily soluble even in cold alcohol. It is insoluble in ether, hot as well as cold. It crystallizes from alcohol in fine concentrically arranged needles, shorter than those obtained from water. From concentrated aqueous solutions there sometimes separate, together with the needles, verrucous masses which led at first to the suspicion that two products had been formed. On recrystallizing these masses, however, from more dilute solutions they separated in the same beautiful needles as the principal portion, and fused at exactly the same point.

Barium sulphamineparatoluate, $(C_6H_3.SO_2NH_2.CH_3.CO_2)_2Ba + 2H_2O$, was prepared from the free acid by boiling with barium carbonate. It crystallizes in concentrically arranged needles which are easily soluble in water. The crystals always attach themselves firmly in hard clumps to the beaker. After drying in the air it was analyzed.

I. 0.2302 gram lost 0.0132 gram H_2O at 200°, and gave 0.0890 gram $BaSO_4 = 0.052332$ gram Ba.

II. 0.359 gram lost 0.0218 gram H_2O at 200°, and gave 0.1385 gram $BaSO_4 = 0.082438$ gram Ba.

		Calculated.		Found.	
				I.	II.
$(C_8H_8SNO_4)_2$	...	428	71.21	...	...
Ba	...	137	22.80	22.73	22.96
$2H_2O$	...	36	5.99	5.73	6.07
		601	100.00		

Calcium sulphamineparatoluate, $(C_6H_3.SO_2NH_2.CH_3.CO_2)_2Ca + 4H_2O$, was prepared by boiling the acid with finely powdered Iceland spar. It is easily soluble in water, and crystallizes from the concentrated solution in very compact, radiating needles, which have a mother-of-pearl lustre. The air-dried salt was analyzed.

I. 0.1950 gram salt lost 0.026 gram H_2O, and gave 0.05 gram $CaSO_4$.

II. 0.22325 gram salt lost 0.02975 gram H_2O, and gave 0.05725 gram $CaSO_4$.

		Calculated.		Found.	
				I.	II.
$(C_8H_8SNO_4)_2$	...	428	79.26	...	...
Ca	...	40	7.41	7.55	7.54
$4H_2O$	...	72	13.33	13.33	13.33
		540	100.00		

Manganese sulphamineparatoluate, $(C_6H_3.SO_2NH_2.CH_3.CO_2)_2Mn + 5H_2O$, was prepared from the acid and manganese carbonate. It crystallizes in small needles from water, in which it is readily soluble. The salt was analyzed after being dried in the air.

I. 0.1785 gram salt lost 0.02825 gram H_2O, and gave 0.02425 gram Mn_3O_4.

II. 0.167 gram lost 0.02525 gram H_2O, and gave 0.02175 gram Mn_3O_4.

		Calculated.		Found.	
				I.	II.
$(C_8H_8SNO_4)_2$	...	428	74.70	...	...
Mn	...	55	9.60	9.79	9.67
$5H_2O$	...	90	15.70	15.83	15.59
		573	100.00		

Oxidation of Cymenesulphamide.

As the preparation of pure paraxylene in quantity involves considerable difficulty, it appeared advisable to employ in our experiments some other hydrocarbon belonging to the para-series. Recent experiments, particularly those of von Gerichten,* have shown that, when chlorine, bromine, nitric acid and sulphuric acid act directly upon cymene, they replace a hydrogen-atom situated in the ortho-position with reference to the methyl-group, and that

* Berichte d. deutsch. chem. Gesell. 11, 1586.

the substitution-products thus obtained yield, by oxidation, derivatives of paratoluic acid in which the methyl-group still occupies the ortho-position with reference to the substituting atom or group. It hence seemed probable that by starting from cymene the same sulphamineparatoluic acid would be obtained as that described above and obtained directly from paraxylene itself. Experiment confirmed this view, and we were thus enabled to prepare sulphamineparatoluic acid without difficulty and in large quantity.

Pure cymene was heated on a water-bath with an equal volume of common concentrated sulphuric acid, a little fuming acid being finally added to effect complete solution. The amide was made from the sodium salt of the sulphonic acid, and was found to possess the properties ascribed it by Berger* and by Jacobsen.† The fusing point was, however, found to be constant at 113-114° (*uncorrected*), whereas previous observers have found it to be 112°.

The purified cymenesulphamide was treated with the chromic acid mixture in the following proportions: 1 part amide, 5 parts potassium pyrochromate and 7 parts concentrated sulphuric acid diluted with three times its volume of water. The mixture was heated for about three hours, first on the water-bath and finally over a free flame. On cooling the oxidation-product separated out, looking exactly like that obtained from paraxylene. The liquid was diluted and filtered. There was obtained upon the filter a mixture consisting of white needles and greenish, apparently amorphous lumps. The mass was treated several times with a cold dilute solution of sodium carbonate until nothing remained but the green lumps. Hydrochloric acid precipitated from the alkaline solution a white substance which was purified by recrystallization from water. The product is thus obtained in the form of long colorless needles fusing at 267° (uncorr.) and having all the properties of sulphamineparatoluic acid as described above.

The green lumps referred to appear to be a peculiar compound of the amide with oxide of chromium. Alcohol dissolves the substance completely, forming a green solution. On the addition of water to this solution a precipitate is formed. As the substance did not present strong evidence of its own purity it was not analyzed. It is insoluble in hydrochloric acid. If the alcoholic solution be boiled for a long time with a large amount of water, and then filtered, a colorless solution is obtained and this yields the pure

* Berichte d. deutsch. chem. Gesell. 10, 976. † Annalen der Chemie, 184, 194.

amide. The green residue is now soluble in hydrochloric acid. This indicates that the green compound though not decomposed by hydrochloric acid is broken up if boiled with a large quantity of water.

The only products formed by oxidation of cymenesulphamide are sulphamineparatoluic acid and the compound of the amide with chromium oxide.

Transformation of Sulphamineparatoluic Acid into the corresponding Oxy-Acids.

As Flesch has shown* that the sulphonic acid obtained by direct action of sulphuric acid in cymene yields an oxytoluic acid identical with one subsequently prepared by von Gerichten† and called by him *a*-oxyparatoluic acid, it was in the highest degree probable that our sulphamineparatoluic acid would yield the same oxy-acid when fused with potassium hydroxide. The fusion was performed in the usual manner in a silver crucible. On dissolving the mass in water and adding hydrochloric acid a precipitate was formed. This was dissolved in a large amount of boiling water, in which it was found to be very difficultly soluble, some animal charcoal added and the solution filtered. After several crystallizations the substance was obtained in the form of a white crystallized powder. This does not fuse at 300°, but sublimes somewhat above this temperature without fusing. With ferric chloride its solution gives a violet-red color. These properties are the same as those given by Burkhardt‡ for oxyterephthalic acid. A close comparison showed that the two substances are identical. Oxidation of the oxytoluic acid is thus seen to be effected by the fusing potassium hydroxide.

The mother-liquor from which the oxyterephthalic acid is precipitated by hydrochloric acid yields on evaporation to a small volume a substance crystallized in needles. This was purified by boiling with animal charcoal and recrystallizing, and then converted into the corresponding lead salt, which was recrystallized from water and easily obtained pure. The salt crystallizes in long, transparent needles having a brilliant lustre. It corresponds to the lead salt of oxyparatoluic acid first prepared by Flesch§ and more recently by von Gerichten.‖ The analyses of the salt showed, however, that, as obtained by us, it contains 1½ molecules of water of crys-

* Berichte d. deutsch. chem. Gesell. 6, 481. † Ibid. 11, 1586. ‡ Ibid. 10, 144.
§ Loc. cit. ‖ Loc. cit.

tallization instead of 2 as found by von Gerichten. It must be remarked that the only analyses of this salt hitherto published by von Gerichten do not give results agreeing very closely with those calculated for 2 molecules of water. The calculated percentage of water for a salt containing 2 molecules is 6.61, while von Gerichten found* 5.85 and 6.04 per cent. A salt with $1\frac{1}{2}$ molecules requires 5.04 per cent. and with this the results of our analyses agree very closely.

I. 0.24 gram salt lost at 130° 0.012 gram H_2O and gave 0.13485 gram $PbSO_4$.

II. 0.2033 gram salt lost at 130° 0.0104 gram H_2O.

		Calculated.		Found.	
				I.	II.
$(C_8H_7O_3)_2$	...	302	56.34	...	...
Pb	...	207	38.62	38.38	...
$1\frac{1}{2}H_2O$	...	27	5.04	5.00	5.11
		536	100.00		

The acid was separated from the salt and found to fuse at 205° (*uncorrected*), while von Gerichten and Rössler state it to be at 203-204°. It crystallizes in needles which are difficultly soluble in cold, but easily soluble in hot water. Ferric chloride produces no color in its solution. It is difficultly volatile with water vapor. From a careful comparison of the acid with the *a*-oxyparatoluic acid now known, we can conclude that the two are undoubtedly identical. But von Gerichten† has shown that in *a*-oxytoluic acid, the hydroxyl group is in the ortho position with reference to the methyl group. Hence it follows, that in sulphamineparatoluic acid the sulphamide group and the methyl are in the ortho position with reference to each other, while, as the acid is derived from paraxylene, it further follows that the methyl and carboxyl are in the para position with reference to each other.

The structure of the acid is thus found to be in accordance with the view expressed when the substance was first discovered, and another illustration is given of the correctness of the law which lies at the foundation of the phenomena which are here being subjected to investigation. *The negative group protects the hydrocarbon residue*, preventing its oxidation by chromic acid.

Another curious conclusion which this investigation helps to

* Berichte d. deutsch. chem. Gesell. 11, 706. † Loc. cit.

establish, though full attention has previously been called to the subject by von Gerichten, is that when negative groups enter into cymene, they take the meta position with reference to the larger residue, propyl. This has been found to be true of Cl, Br, NO_2, SO_3OH. In one of the earlier papers* of this series attention was called to a similar fact in connection with paraethyltoluene. It was shown that when bromine acts upon this hydrocarbon, and the product oxidized, a bromparatoluic acid is obtained. The belief was expressed that in this case it would be found that the bromine exerts a protective influence upon the methyl group. The subsequent determination of the structure of the bromparatoluic acid proved the correctness of the first belief.

Sulphoterephthalic Acid.

The experiments in the meta-series have shown that when the monobasic sulphamine acid is treated with potassium permanganate in neutral solution, the sulphamide group is converted into the sulpho-group and a tribasic acid, sulphoisophthalic acid, is formed. It was hence thought probable that sulphamineparatoluic acid would, under the same treatment, yield sulphoterephthalic acid. Indeed a salt very similar to the acid potassium salt of sulphoisophthalic acid was found in the residues from the oxidation of the mixture of xylenesulphamides, and the same salt was again obtained when a little sulphamineparatoluic acid was subjected to the action of potassium permanganate. The nature of the salt was not determined, however, owing to a lack of material. It has now been prepared in larger quantity and its nature determined. It is *sulphoterephthalic acid.*

The substances were brought together in the following quantities: 1 gram sulphamineparatoluic acid, 5 grams potassium permanganate and 100 c. c. water. The mixture was heated in a flask on a water-bath for about 7 to 8 hours. There remained a slight excess of the permanganate which was reduced by means of a few drops of alcohol. The solution was then filtered, concentrated and treated with hydrochloric acid. A white crystalline precipitate was formed. This was recrystallized from water and thus easily obtained in perfectly pure condition. From a concentrated solution it crystallizes in long transparent needles, from a dilute solution it separates in well-developed plates which are large enough to admit

*On the Oxidation of Bromparaethyltoluene. This Journal, 1, 138.

of measurement. The salt is difficultly soluble in cold water, particularly if hydrochloric be present, though in warm water it is quite easily soluble. The substance was repeatedly tested for nitrogen by fusing it with sodium and then treating with a partially oxidized solution of ferrous sulphate. Not a trace of a blue precipitate was obtained from the purified salt, and the conclusion is justified that it contains no nitrogen. The analyses gave the following results:

I. 0.3018 gram lost at 150° 0.0182 gram H_2O, and gave 0.0867 gram K_2SO_4.

II. 0.6641 gram lost at 150° 0.0399 gram H_2O, and gave 0.1916 gram K_2SO_4

		Calculated.		Found.	
				I.	II.
$C_8H_5O_7S$	...	245	81.10	...	...
K	...	39.1	12.94	12.89	12.95
H_2O	...	18	5.96	6.03	6.00
		302.1	100.00		

The results agree closely with those required by a salt of the formula, $C_6H_3\begin{cases}CO_2H\\CO_2H\\SO_3K\end{cases}+H_2O$, or *mono-potassium sulphoterephthalate.*

If this is really the formula of the salt, it must still contain two atoms of hydrogen replaceable by metals. To decide this point, weighed quantities of the salt were neutralized with an ammonia solution of known strength.

I. 0.4739 gram salt required for neutralization 31.2 c. c. of an ammonia solution of known strength. The quantity required according to calculation is 30.8 c. c.

II. 0.6101 gram required 39.4 c. c. of the same ammonia solution, whereas the calculated quantity for this amount of salt is 39.6 c. c.

The results of the analyses, and the neutralization experiments taken together with the method of formation, show clearly that the substance under examination is a derivative of sulphoterephthalic acid. The permanganate in this case, as well as in the meta series, converts the methyl group into carboxyl and the sulphamide group into the sulpho-group.

Monohydro-barium sulphoterephthalate, $C_6H_3\begin{cases}CO_2H\\CO_2\diagdown\\SO_3\diagup\end{cases}Ba+H_2O$.

This salt is thrown down in crystalline form when a solution of barium chloride is added to a solution of the potassium salt just described. It is very difficultly soluble in water, hot as well as cold. It cannot be obtained in well-crystallized form from an aqueous solution, though it looks homogeneous and crystalline. A similar salt of sulphoisophthalic acid, containing $1\frac{1}{2}$ molecules of water, was described in an earlier paper. The analyses gave the results here communicated:

I. 0.40345 gram salt lost 0.01815 gram H_2O at 270° and gave 0.2307 gram $BaSO_4$.

II. 0.3246 gram salt lost 0.0148 gram H_2O at 290° and gave 0.1884 gram $BaSO_4$.

III. 0.263 gram salt gave 0.089964 gram $BaSO_4$.

		Calculated.		Found.	
$C_6H_4O_7S$	...	244	61.15	...	...
Ba	...	137	34.34	34.12	34.20
H_2O	...	18	4.51	4.55	...
		399	100.00		

The facts here communicated are sufficient for the present to characterize the new substance, but it will be subjected to further study in order that we may learn more concerning its intimate nature. Dr. William Burney has already investigated a number of its derivatives and has established beyond the possibility of a doubt the character of the relation which it bears to terephthalic acid. The results of his study will soon be published in this Journal.

Terephthalic Sulphinide.

If the *potassium salt* of sulphamineparatoluic acid be treated with potassium permanganate in the manner described above, the result is quite different from that reached when the free acid is used. The same is true if a few drops of a solution of potassium carbonate or hydroxide be added to the oxidizing mixture. Only a small quantity of ammonia is given off and the product contains nitrogen and potassium. The oxidation is conducted in exactly the same way as in connection with the free acid, and the final addition of

hydrochloric acid produces a similar precipitate. This is more difficultly soluble in water than the acid potassium salt of sulphoterephthalic acid, and comes down in different forms. It crystallizes usually in short thick prisms, or from concentrated solutions it is thrown out in glistening flakes, which, however, increase in size as the solution becomes cool. Under some circumstances it crystallizes in forms which are very similar to those taken by the sulphoterephthalate, but, if the solution containing the crystals be allowed to stand for a few days, they pass over into the forms which are characteristic of the new substance.

In addition to the principal product containing nitrogen, only a small quantity of the sulphoterephthalate is formed. If, however, the free acid be oxidized none of the nitrogenous substance is formed, or, at least, none has been found up to the present, though special precautions have been taken for the purpose of finding it.

It was at first thought that the new product is simply a derivative of sulphamineterephthalic acid, $C_6H_3\begin{cases}CO_2H\\CO_2H,\\SO_2NH_2\end{cases}$ but it was soon shown that in all probability it is a substance similar to the one recently described by one of us (R) together with C. Fahlberg,* under the name benzoic sulphinide. This is an inner anhydride of orthosulphaminebenzoic acid, $C_6H_4\begin{cases}CO\\SO_2NH\end{cases}$, obtained as one of the products of the oxidation of orthotoluenesulphamide with potassium permanganate. In sulphamineparatoluic acid there exist the same conditions as those in orthotoluenesulphamide, *i. e.* the sulphamide group occupies the ortho-position with reference to the methyl. Apparently the oxidation takes place in the same way in the two compounds. The analyses led to the following results:

I. 0.2715 gram salt lost 0.0179 gram H_2O at 240°, and gave 0.0831 gram K_2SO_4.

II. 0.5038 gram salt lost 0.0332 gram H_2O at 240°, and gave 0.1514 gram K_2SO_4.

III. 0.4338 gram gave 19.4 c.c. N at 766.5 m.m. pressure at 235°.

IV. 0.4315 gram gave 0.3445 gram $BaSO_4$.

V. 0.5204 gram gave 0.42495 gram $BaSO_4$.

In attempting to determine the formula of the substance from the experimental data here given, a difficulty is met with at once in

* This Journal 1, 426.

connection with the molecule of water which is given off at 240°. Is this to be regarded as water of crystallization? or is it due to the transformation of the original substance into an inner anhydride? If it is water of crystallization then the formula of the substance is $C_6H_3\begin{cases}CO_2K\\CO\\SO_2NH\end{cases}+H_2O$, and it is similar to the product which we have called benzoic sulphinide. If, however, the water is given off from the substance and an anhydride formed, then the formula is $C_6H_3\begin{cases}CO_2K\\CO_2H.\\SO_2NH_2\end{cases}$ We believe that the former view is the more probable, for the reason that, in the case of an isomeric substance belonging to the meta series since obtained,* there are two molecules of water given off together under the same conditions, and, in the light of a simpler explanation, it would be purely gratuitous to assume that one of these molecules represents water of crystallization, and the other water of constitution. The comparison of the results of the analysis with the results calculated for two possible formulas is given below, assuming in each case that there is a molecule of water of crystallization present:

	Calculated for $C_6H_3\begin{cases}CO_2H\\CO_2K\\SO_2NH_2\end{cases}+H_2O$	Found.		Calculated for $C_6H_3\begin{cases}CO_2K\\CO\\SO_2NH\end{cases}+H_2O$
K ...	12.98	13.74	13.49	13.81
N ...	4.64	5.04	...	4.94
S ...	10.62	10.95	11.21	11.30
H_2O ...	5.98	6.58	6.59	6.36

The formula which we ascribe to the substance is $C_6H_3\begin{cases}CO_2K\\CO\\SO_2NH\end{cases}+H_2O$. According to the principle of nomenclature adopted in a previous paper this is the potassium salt of *terephthalic sulphinide*, or, in order to indicate in the name the acid properties, it might be called *sulphinido-terephthalic acid*. Of course this anhydride readily yields salts of sulphamineterephthalic acid, $C_6H_3\begin{cases}CO_2H\\CO_2H,\\S_2O_2NH_2\end{cases}$ hence the potassium salt when dissolved in water must contain a second hydrogen atom replaceable by metals.

* Berichte d. deutsch. chem. Gesell. 12, 1436.

That this is so was conclusively proved by three neutralization experiments.

I. 0.54935 gram required for neutralization 19 c. c. of an ammonia solution of known strength.

II. 0.5526 gram required 19.8 c. c.

III. 0.3972 gram required 14.4 c. c.

These results, when compared with the calculated quantities for the two possible formulas, again show that, if the questionable molecule of water be regarded as water of crystallization, the substance is undoubtedly a derivative of the sulphinide.

Calculated for $C_6H_3\begin{cases}CO_2H\\CO_2K\\SO_2NH_2\end{cases}+H_2O$.	Used.	Calculated for $C_6H_3\begin{cases}CO_2K\\CO\\SO_2NH\end{cases}+H_2O$.
17.9 c. c.	19.0 c. c.	19.0 c. c.
18.3 c. c.	19.8 c. c.	19.3 c. c.
13.1 c. c.	14.4 c. c.	14.4 c. c.

Facts which have been discovered in this laboratory since the above investigation was completed indicate very clearly that the nitrogenous substance obtained, when the oxidation is carried on in an alkaline solution, in reality belongs to the class of bodies designated as sulphinides, and it seems to be a general law that:

Whenever a compound containing the sulphamide group and methyl in the ortho position is oxidized in *alkaline solution*, a sulphinide is formed.

If, on the other hand, the solution is *neutral at the beginning of the oxidation*, as it is when orthotoluenesulphamide is employed, then two products are formed in about equal quantities. One of these is the sulphinide and the other the corresponding sulphonic acid.

If, finally, the solution is *acid at the beginning of the operation*, as it is when free sulphamineparatoluic acid is oxidized, only the corresponding sulphonic acid is formed.

The last result is also reached apparently, if precautions be taken to prevent the formation of free alkali. Thus, in an experiment performed by Dr. Fahlberg, the oxidation was carried on in a vessel through which a constant current of carbon dioxide was conducted. The result in this case was the same as in those cases in which free acids were employed. Complete transformation into the corresponding sulphonic acid took place. According to this, we can

control the nature of the product by very simple means. If, in oxidizing with potassium permanganate a sulphamide compound containing a hydrocarbon residue in the ortho position, we desire the corresponding sulphinide, a little potassium carbonate or hydroxide is added to the oxidizing mixture. If we desire the sulphonic acid, precautions must be taken to prevent the formation of free alkali, at least at an early stage of the process, and the simplest way to prevent this is to keep the vessel filled with carbon dioxide. These general statements are, it must be confessed, based on too small a number of experiments to warrant their final acceptance without further verification. It is hoped that experiments now in progress in this laboratory will furnish the required testimony.

APRIL, 1880.

REVIEWS AND REPORTS.

BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

(Continued from Vol. I, p. 449.)

MANUFACTURE OF GLASS.

Materials.—Improvement has of late years been observable in the more general use of comparatively pure materials, even the sand being, in consequence of cheapened transportation, more carefully selected than formerly; but especially have the alkalies been obtainable in much purer forms and at lower prices. As the result of this, colorless glass has noticeably replaced for many common purposes, as in the case of most apothecaries' bottles for dispensing medicines, perfumery, etc., the coarser "green glassware" formerly in use. There has also been improvement in the pains bestowed upon ascertaining and using the best proportions of the materials with a view to homogeneity and definiteness of composition in the glass, thus diminishing the risk of "devitrification" and ready alteration of the surface of the glass in use by water or other reagents. There seems, however, to be still room for advance in this direction, both as to investigation and application of its results in practice. Of comparatively new materials used, zinc oxide in Belgium and barium carbonate in France and the north of England hardly deserve to be considered as more than experimental additions.

Furnaces.—Decidedly the most important improvement made for a long time in the manufacture of glass has been the adaptation to this special use of the Siemens regenerative furnace with gaseous fuel. Originally arranged to work with glass pots of the types long in use, the furnace in its improved form, designed by Siemens, dispenses with the use of these vessels altogether, thereby saving much expense, labor and risk, and provides for the complete preparation of the glass in the hearth itself, this being divided into three compartments, in the first of which the mixture of raw materials is fused, in the second the glass is "fined" or cleared, and in the third it is brought down to the proper temperature and therefore consistence for working.

Except perhaps iron puddling and steel making, no application of this valuable invention brings out more prominently its peculiar merits — the continuous action, crude material going in at one end and finished glass coming out of the other; the purely gaseous atmosphere of the hearth, free from soot or ash; the extremely high temperature readily obtainable, affording the means of perfect fusion and easy separation of sand grains, gas bubbles, &c.; the effective mixture of the molten glass as it flows under and over the partition walls of the hearth; and the complete command of temperature for working purposes, both of the glass itself and of the working openings for reheating.

Processes of Glass Working.—For the production of glass in sheets for windows, the "crown glass" process of "flashing," long a distinctively English industry, has almost completely ceased to be employed, while in its place the "cylinder" process has undergone marked extension and improvement as to the scale upon which its product is turned out, the size of the sheets made by it—reaching even to 84x42 inches — and the smooth, even condition of the surface of the flatted sheets. Plate glass too has been brought more and more widely into use, both in the original form of sheets polished on both sides after casting, and perhaps still more largely with rough surfaces as taken from the casting table, and with flutings and other figures embossed, or perforations made beneath the roller. Immense plates, extending up to more than 20x10 feet, have become familiar to us, the limit of size being found in fact more in the difficulty of safely moving and setting in place such magnificent slabs than in that of originally producing them. In the manufacture of hollow ware perhaps the most noteworthy change has been the growth of the process of pressing in moulds without blowing. The development of this especially American industry has been rapid, and marked by much varied ingenuity as to the details of the moulds and other tools.

Annealing.—Beside minor improvements in the construction of kilns for ordinary annealing with movable soles or floors, a marked novelty has been the introduction by De la Bastie and others of the practice of rapid cooling of articles of glass to a temperature still much above that of the atmosphere, giving rise to the manufacture

of the so-called "hard glass" or "toughened glass," in the production of which the articles to be treated are, at a low red heat or a temperature just low enough to secure rigidity, plunged suddenly into a bath of heated oil, glycerine or other suitable material.

The process of Pieper, involving exposure of the hot glass to a current of superheated but colder steam, and that of F. Siemens, forcing the glass into hollow moulds, generally of metal, kept at determinate temperatures in their different parts by the circulation of water, while actual contact with the face of the mould is prevented by the interposition of a layer of wire gauze or other material, produce essentially the same sort of effect. For some purposes the resulting great increase in strength of the glass, its capability of withstanding greater mechanical stress and more violent blows, is undoubtedly valuable, but it seems likely that the expectations at first entertained as to the usefulness of the new product will turn out to have been exaggerated. Its unmanageable character as to any modification of dimensions, shape or surface by cutting with a diamond or by grinding, its complete, even dangerous, shattering when it does break, and the difficulty of securing uniform results from the tempering under varying conditions of size and shape of the articles treated, are all serious disadvantages, though perhaps not altogether incapable of being overcome by further modifications of the process. The very recent and rather startling proposal of F. Siemens to make railway sleepers of toughened glass, aside from any special difficulties or dangers, does not seem likely to be altogether free from the same objections arising from excessive jarring vibration and consequent wear and tear of rails and rolling stock, which caused the granite blocks used in the early days of railway construction to be laid aside.

Optical Glass.— The progressive improvement in this difficult branch of the manufacture, continued for a good many years past and still going on, is best evidenced by the steady increase in the size of the disks, now obtainable up to more than thirty inches in diameter, from which the largest telescope lenses are made, while clearness, uniformity and freedom from flaws of any kind of these great lenses have also been secured in higher degree than formerly. Chemically the chief novelty in the composition of this kind of glass has been the introduction of thallium silicate into flint of unusual density, but this has been practised upon a very limited scale only.

Decoration of Glass Work.—There has been of late years some advance in the clearness and brilliancy of colored glass for windows, but more marked results have been attained in the artistic than the technical treatment of this material. The revived imitations of the *defects* of ancient colored glass, such as imbedded sand-grains, air bubbles and the like, form a curious feature of its recent history.

The imitations in glass of the various precious stones are made of late with remarkable fidelity to natural appearance, and

some of the specimens sold are noticeable for a degree of hardness, much less, it is true, than is usually claimed for them by dealers, but much exceeding anything that was known some years ago.

Well deserving the attention they have received have been the beautiful products of the revived glass industry at Murano, especially the delicate "ritorto" work, depending on the plastic union of symmetrically disposed rods of variously colored glass and the twisting of the mass they produce as it is afterwards developed into the desired form. Not only under Salviati at Murano, but more recently in Austria has this mode of decoration been admirably applied to the reproductions of early forms as well as to designs of modern origin.

To the older varieties of "milk glass" or enamel has been added the "hot-cast porcelain" made by fusing together quartz sand, cryolite and zinc oxide, chiefly used so far for the rougher and less artistic articles which admit of being made from such material.

In surface enamelling of sheet glass may be noted the transfer of lace patterns from the woven or netted fabric itself, used as a stencil to distribute the pulverized enamel upon the surface, afterwards to be burnt on.

The most valuable novelty in the surface alteration of glass is the process of etching by means of Tilghman's sand-blast. The simplicity and quickness of the process, the great depth to which the abrasion of the glass may readily be carried, cutting through, for instance, a flashing of colored glass or even producing complete perforation, the applicability of the method to sheets of glass so large as to be treated with great difficulty, if at all, by the older grinding-wheel or by hydrofluoric acid, and the delicacy with which the minute features of intricate designs may be engraved — admirably shown in some of the etchings of photographs upon a film of chromated gelatine covering the glass — approve the process as one of great and permanent value.

Amongst the latest modifications of glass decoration is the "iridescent glass" exhibiting a delicate play of soap-bubble colors, the result of slight chemical attack of the surface by moderately strong liquid hydrochloric acid under pressure in close vessels, or by the fumes from chloride of tin or analogous material volatilized in a reheating furnace.

The silvering of glass by deposition of metallic silver from its solutions by means of such reducing agents as glucose, milk sugar, aldehyde, tartaric acid, etc., has completely passed from the laboratory to the workshop, where it is now regularly and extensively practised. A somewhat recent improvement consists in increasing the density of the film of silver, and at the same time removing the unpleasant yellow tinge which it is apt to have, by moistening the surface with a dilute solution of mercuro-cyanide of potassium, so as to form a silver amalgam.

Dodé's process for platinizing glass, by carefully heating it after the surface has received a nicely applied thin coating of platinic

chloride mixed with one of the essential oils, has the advantage of furnishing a mirror which reflects from the front face, avoiding the double passage of light through the glass itself, while the exposed metal is not liable to tarnish. It does not seem to have been generally noticed that a simple piece of flat sheet glass treated in this way, and supported at a suitable inclination, makes quite an effective *camera lucida*, as the platinum film is thin enough to permit of the pencil and hand of the draughtsman being seen through it, while at the same time the objects to be copied are seen by reflection.

Glass drawn out into extremely fine threads—the so-called "glass wool"—has of late, in the hands of a Viennese firm, been used for decorative purposes of a better sort than the long known toys turned out at the glassblower's lamp, and has also been produced in useful shape as a material for filtration.

Manufacture of Porcelain and other Clay-Ware.

It is more difficult to point out marked changes in this industry than in that of glass in matters connected with chemistry: the materials used being mixtures of more complex character, and the extent and manner of their union in the baking varying with the mode in which the heat is applied, the chemistry of both processes and products is less advanced. More attention has been given to mechanical improvements in grinding, mixing, etc., to the methods of burning, and especially to artistic expression in design and decoration. Still progress has unquestionably been made in the former direction within the last few years.

General Character of Products.—On the whole, probably the greatest improvement has been in the higher grades of stoneware and earthenware, rather than in porcelain itself. Almost the same care bestowed upon the production of the latter has of late been given to the treatment of the former, the selection of the materials, their subdivision, careful kneading together, moulding, drying, burning and glazing. Special kinds of ware have attracted particular attention from time to time, partly from the intrinsic character of the mass, partly from the designs which it has been used to carry out, such as the revived Majolica and Persian ware of Minton and the Parian and other biscuit ware of Copeland and others. The excellent common stoneware now made, strong and capable of bearing much in the way of change of temperature and exposure to energetic chemical reagents, has done valuable service as material for many of the vessels used in manufacturing chemistry.

Mechanical Appliances.—The most valuable of these brought into use in comparatively recent times has probably been the strong and effective filter press, which has done so much good service in connection with general chemical manufactures, and which is now largely used in removing the surplus water from the clay after the process of mixing. Special features introduced

in some of these presses tend to prevent as far as possible the enclosure of air bubbles, which would lead to flaws in the ware when burnt.

Kilns.—The regenerative gas furnace has begun to lend its valuable aid to this manufacture as well as to that of glass, and with marked advantage, including much saving of fuel and reduction of the number of pieces of ware spoiled in the firing. In this application of the furnace there is room for careful study of the distribution of the heat, dependent on the arrangement of the gas and air flues, in order to secure uniformity of firing throughout the contents of the kiln, varying as these do in form and size.

Decoration.—The feature of most note in this direction has of late perhaps been the extension of the transfer of *printed* patterns and designs, replacing to a large extent painting by hand. The method in question has long been in use for coarser purposes, but now much better work is done, and the production of effects in several colors by the well-known method of superposition—"color printing"—is commonly and extensively practised. Metallic "lustres" too are applied with more successful effect than formerly, and the peculiar surface appearance, resembling that of mother-of-pearl, given by a lustrous bismuth glaze, has been introduced.

J. W. MALLET.

(*To be continued.*)

REPORT ON PROGRESS IN ANALYTICAL CHEMISTRY.

(*Continued from p. 367.*)

Hydrogen.—W. Hempel* finds that the free hydrogen contained in any mixture of hydrogen, marsh gas and nitrogen can be determined by mingling with air and conducting the mixture over superficially oxidized palladium sponge. If care is taken to keep the temperature below 200°, the marsh gas is wholly unaffected, while the free hydrogen is completely oxidized.

A. Lionel† recommends the use of the black oxide of copper for the purification of hydrogen gas. It completely arrests, even at ordinary temperatures, hydrochloric acid, and the compounds of hydrogen with sulphur, selenium, phosphorus, arsenic, antimony and silicon, but not the hydrocarbons. The oxide to be used for this purpose is best prepared by treating the sulphate of copper with caustic potassa and drying the precipitate at 100°.

Oxygen.—F. Fischer‡ describes an apparatus for the determination of the oxygen of the air by means of heated copper wire.

F. Tiemann and C. Preusse§ describe in detail, and with some modifications of their own, the three methods which have been proposed for the quantitative determination of the oxygen absorbed

* Ber. d. d. ch. Ges. 1879, 1006.
† Comptes rendus, 89, 440.
‡ Ber. d. d. ch. Ges. 1879, 1696.
§ Ibid. 1879, 1768.

in water; namely, the gas-volumetric, the volumetric of Schützenberger and Risler, and that of Mohr. They also give the results which they obtained by a comparative examination of the three. The quantities obtained by the first two are nearly equal and quite correct, while those by the last are uniformly too small.

Water.—H. Pellet* describes his method of determining the several varieties of nitrogen contained in natural waters. It is similar to that lately proposed by Lechartier.†

F. Tiemann and C. Preusse‡ have brought together again the several methods in use for the estimation of the organic matter in water. Their own experiments tend to prove the superiority of Kubel's method over that of Fleck; also, that organic matter in considerable quantities is lost during the evaporation of an impure water.

Chlorine.—R. Nolte§ states that when grains are incinerated, a part and in some cases the whole of the chlorine is lost in consequence of the decomposition of the chlorides by phosphoric acid. To remedy this the author incinerates in the presence of carbonate of sodium.

G. Fraude‖ recommends perchloric acid as a reagent for the detection of certain alkaloids.

Iodine.—O. Schott,¶ "On the Determination of Iodine in Varec."

To determine iodine volumetrically E. Allary** employs a standard solution of bromide and bromate of potassium, instead of hyposulphite of sodium. The iodide against which the solution is to be standardized, or in which the iodine is to be determined, is treated with starch paste and hydrochloric acid, and the solution of bromide and bromate allowed to flow in from a burette. The hydrochloric acid, bromide and bromate react as follows:

$$5KBr + KBrO_3 + 6HCl = 3H_2O + 6KCl + 6Br.$$

The bromine thus liberated sets free an equivalent amount of iodine—$6Br + 6MI = 6MBr + 6I$. These reactions continue until the iodide has been completely decomposed, and at that point the blue color imparted to the starch attains its maximum intensity. If, now, more of the solution of bromide and bromate is added, the free bromine combines with the iodine and the blue color gradually diminishes to a minimum.

Sulphur.—J. Fletcher†† states that sulphide of hydrogen may be easily prepared for laboratory purposes by fusing together sulphur and paraffine. W. Johnstone‡‡ remarks that he made use of this method for some time, but gave it up in consequence of the explosive properties of the mixture.

C. Fahlberg§§ has replied to Delachanal and Mermet,‖‖ and

* Comptes rendus, 89, 523.
† This Journal, 1, 285.
‡ Ber. d. d. ch. Ges. 1879, 1906.
§ Comptes rendus, 89, 955.
‖ Ber. d. d. ch. Ges. 1879, 1558.
¶ Zeitsch. an. Ch. 18, 443.
** Bull. de la Soc. Chim. 32, 273.
†† Chem. News, 40, 154.
‡‡ Chem. News, 40, 167.
§§ Ber. d. d. ch. Ges. 1879, 2303.
‖‖ This Journal, 1, 288.

shown that the method devised by Iles and himself is essentially different from that proposed by these authors.

T. Nakamura* determines the sulphur in coal by mixing the finely pulverized material with carbonate of sodium or carbonate of sodium and potassium, and heating below redness. The coal is rapidly oxidized without evolution of smoke.

To determine the sulphur contained in sulphides A. Colson† burns in a current of oxygen, and absorbs the products of the combustion in a solution of caustic soda of known strength. This solution is afterwards diluted to a known volume, and the sulphite contained in a measured portion of it determined by means of iodine. To another equal portion sufficient iodine solution to convert the sulphite into sulphate is added, and the excess of alkali then estimated by means of standard sulphuric acid. Allowance is made in the calculation of results for the fact that each atom of iodine neutralizes one molecule of caustic soda:

$$2NaOH + I_2 + Na_2SO_3 = Na_2SO_4 + H_2O + 2NaI.$$

According to A. Rollet‡ the sulphur contained in iron, steel, ores, slags and fuel can be readily and completely converted into sulphide of hydrogen by placing the material in a porcelain tube and heating it to redness in a current of gas, consisting of three-fourths of hydrogen and one-fourth of carbon dioxide. The author absorbs the sulphide of hydrogen thus produced in a solution of silver nitrate. When it is desired to determine the sulphur contained in a gas, the material is mingled with carbon dioxide or hydrogen according to the quantity of oxygen which it contains, and then passed through the heated porcelain tube.

Nitrogen.—H. Ritthausen,§ "On the Nitrogen contained in Vegetable Albumenous Compounds, as determined by the Method of Dumas and that of Will and Varrentrapp."

A. R. Leeds,‖ "On the Determination of Nitrates in very dilute Solutions."

R. Warrington,¶ "On the Determination of Nitric Acid by Means of Indigo, with special Reference to Water Analysis."

A. Wagner,** "On the Formation of Nitric Oxide by Decomposition of Saltpeter at red Heat."

E. Pfeiffer,†† "On Persoz's Method of estimating Nitric Acid."

In order to detect nitric in the presence of nitrous acid, A. Piccini‡‡ destroys the latter by means of urea and sulphuric acid. The solution may then be tested for nitric acid by adding zinc, iodide of potassium and starch.

J. Tschelzoff,§§ "On the Determination of Nitrogen in Explosive Nitric Esters."

P. Griess‖‖ has described a new reaction by which the minutest

* Jr. Ch. Soc. 1879, 785.
† Bull. de la Soc. Chim. 32, 115.
‡ Dingler's Jour. 233, 124.
§ Z. an. Ch. 18, 601.
‖ Z. an. Ch. 18, 428.
¶ Jr. Ch. Soc. 1879, 578.
** Z. an. Ch. 18, 552.
†† Z. an. Ch. 18, 597.
‡‡ Ber. d. d. ch. Ges. 1879, 1928.
§§ Ber. d. d. ch. Ges. 1879, 1486.
‖‖ Ber. d. d. ch. Ges. 1879, 427.

traces of nitrous acid may be detected. The solution containing the nitrite is acidified with sulphuric acid, and then treated with a small quantity of a solution of sulfanilic acid. After the lapse of about ten minutes a few drops of a solution of naphtylamine sulphate, from which the color has been removed by animal charcoal, are added. A fine red color is developed. By means of this reaction the presence of nitrous acid in the saliva may be detected.

Phosphorus.—E. Wein,* with the assistance of L. Rösch and J. Lehmann, has made a careful examination of the different methods proposed for the extraction of the soluble phosphoric acid in superphosphates; and concludes that the usual practice of digesting 20 grams of the material for two hours with one liter of cold water gives the best results.

O. Schlickum† proposes a new method for the alkalimetric determination of phosphoric acid, which is based on the fact that a solution of this acid containing cochineal becomes reddish-violet in color as soon as one atom of hydrogen in each molecule has been replaced by a metal.

Arsenic.—F. Selmi,‡ "On Schneider's Method of Separating Arsenic in Cases of Poisoning."

Antimony.—F. P. Dewey,§ "On Clarke's Method for the Separation of Tin from Arsenic and Antimony."

Bismuth.—M. Kuhara,‖ "A Method for Estimating Bismuth Volumetrically."

R. Schneider,¶ "On the Conduct of Bismuth containing Arsenic towards Nitric Acid, and on the Preparation of basic Nitrate of Bismuth free from Arsenic."

Carbon.—S. Kern,** "On the Determination of Carbon in Cast-Steel."

W. D. Herman,†† "On the Determination of Carbon in Steel."

J. C. Smith,‡‡ "A Device for the rapid Filtration of the Carbon in Cast-Iron and Steel Analyses."

F. Landolph,§§ "On the Analysis of organic Compounds containing Fluorine and Boron."

W. Hempel‖‖ has made some experiments on the limits of the detection of carbonic oxide; and, incidentally, on the quantity of it required to produce symptoms of poisoning. Mice were placed between two funnels whose edges were fastened together by means of a rubber band, and air containing known percentages of carbonic oxide drawn through the apparatus. The blood of the animals was then subjected to spectroscopic examination as prescribed by Vogel. In this manner it was found possible to detect the carbonic oxide when the air experimented upon contained only .03 per cent. Decided symptoms of poisoning were observed as soon as the

* Liebig's Annalen 198, 290.
‡ Ber. d. d. ch. Ges. 1879, 1699.
‖ This Journal, 1, 326.
** Chem. News, 40, 225.
‡‡ This Journal, 1, 368.
† Ber. d. d. ch. Ges. 1879, 2253.
§ This Journal, 1, 244.
¶ Jr. für prak. Ch. 20, 418.
†† Chem. News, 40, 263.
§§ Ber. 1879, 1586.
‖‖ Z. an. Ch. 18, 399.

proportion of carbonic oxide was increased to .05 per cent. Experiments were also made upon the spectroscopic detection of carbonic oxide in diluted blood, through which air containing it had been drawn. The latter method, however, was found to be less sensitive than the former. When the air contained less than .05 per cent. the blood failed to give the characteristic reaction.

A. Wagner* has found that when carbon dioxide is passed over heated stannous oxide, the former is reduced to carbonic oxide, and the latter oxidized to stannic oxide.

K. Birnbaum and M. Mahn,† "On the Conduct of Anhydrous Oxide of Calcium towards Carbonic Anhydride."

M. Kapusstin,‡ also G. Lunge,§ "On the Determination of the Carbon Dioxide of the Air."

A. Gawalovski,‖ "Gasvolumetric Estimation of Carbonic Acid."

Potassium.— H. Precht,¶ "The Determination of Potassium as double Chloride of Potassium and Platinum."

W. Knop and Hasard,** "Determination of Alkalies in Silicates."

Lithium.—G. Merling†† describes some experiments on the compounds of lithium with phosphoric acid, which tend to establish the accuracy of the method of determining lithium as phosphate.

Calcium.—J. Stingl,‡‡ "On the Valuation of Burned Lime."

Magnesium.—A. Classen§§ determines magnesium in the following manner: The solution, whose volume should be about 25 cc., is treated with a saturated solution of ammonium oxalate until whatever precipitate is produced is redissolved. It is then heated to boiling; and an equal volume of 80 per cent. acetic acid added; the boiling is continued for some minutes with constant agitation; after which the whole is allowed to stand six hours at a temperature of about 50°. The precipitate is separated by filtration, washed with a solution consisting of equal volumes of strong acetic acid and alcohol, and finally converted into oxide by heating in a platinum crucible. If it is desired to separate magnesium from the alkalies by this method, it is necessary to make the solution more dilute (50 cc. instead of 25), and to employ a less concentrated solution of ammonium oxalate (1 part of the salt dissolved in 25 parts of water), also to add a quantity of alcohol equal to about one-third of the volume of the liquid.

In order to determine magnesium volumetrically, H. Precht‖‖ treats the solution containing it with a measured quantity of a standard solution of caustic potassa, dilutes to a known volume, allows the magnesium hydroxide to subside, and estimates the excess of the alkali in a measured portion of the liquid by means of a standard acid.

Zinc.—F. Selmi,¶¶ "On the Conduct of Zinc towards Phosphorus, Phosphide of Hydrogen, Sulphide of Hydrogen and Iron Salts."

* Z. an. Ch. 18, 559.
† Ber. d. d. ch. Ges. 1879, 1547.
‡ Ber. 1879, 2376.
§ Dingler's Journal, 231, 331.
‖ Z. an. Ch. 18, 560.
¶ Z. an. Ch. 18, 509.
** Z. an. Ch. 18, 462.
†† Z. an. Ch. 18, 563.
‡‡ Z. an. Ch. 18, 501.
§§ Z. an. Ch. 18, 373.
‖‖ Z. an. Ch. 18, 438.
¶¶ Z. an. Ch. 18, 471.

J. B. Schober * determines zinc volumetrically by adding to its solution a measured quantity of a standard solution of an alkaline sulphide and, then, of silver nitrate; after which the excess of silver is estimated by Volhard's method.

A. Classen † determines zinc by precipitation as oxalate in precisely the same manner as magnesium, except that neutral potassium oxalate is used instead of the ammonium salt. The method ‡ may be employed for the separation of zinc from iron and aluminium.

Copper.—By this method § copper, also, may be determined and separated from iron aluminium.

W. Ohl,‖ "On the Electrolytic Determination of Copper, etc."

Nickel.—According to A. Classen¶ the oxalate method is also applicable to the determination of nickel and its separation from iron and aluminium.

W. Ohl,** "The Electrolytic Determination of Nickel, etc."

E. Donath†† bases on the different conduct of nickel and cobalt towards iodine a method of determining the two when they occur together. The solution containing the metals is divided into two equal portions. One is treated with caustic potassa and bromine; the other, with caustic potassa and iodine. In the first case both nickel and cobalt are converted into sesquioxides; in the second, only the cobalt. The precipitates are finally treated with hydrochloric acid and the quantity of chlorine liberated by each determined by the iodine method.

P. Dirvell‡‡ separates the two metals by adding to their solution a mixture of a solution of acid carbonate of ammonium and of a phosphate, and gently warming. Cobalt is precipitated but not nickel.

Cobalt—W. Ohl,§§ "On the Electrolytic Determination of Cobalt, etc."

Cobalt, according to Classen,‖‖ can also be quantitatively precipitated and separated from iron and aluminium by means of oxalate of potassium and acetic acid.

Iron.—R. Schœffel,¶¶ "The Determination of Chromium and Tungsten in Steel and Iron Alloys."

J. Jewett,*** "Influence of Acetic Acid on the Separation of Iron as Basic Acetate from Manganese, Zinc, Cobalt and Nickel."

P. Derome††† states that phosphoric acid may be separated from the oxides of iron and aluminium by strongly heating the material, mixed with five or six times its weight of dried sulphate of sodium, eight or ten minutes before the blast lamp.

T. Twynam,‡‡‡ "Method for the Estimation of the Oxide of Iron and Alumina in Commercial Phosphates."

* Z. an. Ch. 18, 467.
† Z. an. Ch. 18, 189.
‡ Z. an. Ch. 18, 381.
§ Z. an. Ch. 18, 388.
‖ Z. an. Ch. 18, 523.
¶ Z. an. Ch. 18, 189, 379, 386.
** Z. an. Ch. 18, 522.
†† Ber. d. d. chem. Ges. 1879, 1868.
‡‡ Comptes rendus, 89, 903.
§§ Z. an. Ch. 18, 523.
‖‖ Z. an. Ch. 18, 189, 379, 384.
¶¶ Ber. d. d. ch. Ges. 1879, 1863.
*** This Journal, 1, 251.
††† Comptes rendus, 89, 952.
‡‡‡ Chem. News, 40, 203.

Manganese.—F. Beilstein and L. Jawein* propose two methods for the direct separation of manganese and iron. By the first, the metals are converted into soluble potassium-mangano- and ferrocyanides, and the manganese then precipitated by means of iodine. By the second they are dissolved in strong nitric acid and chlorate of potassium added. The manganese is completely precipitated, but always contains a small quantity of iron.

J. Volhard† has published an investigation of unusual interest and importance on the separation and determination of manganese. He finds that the volumetric method of determining manganese by permanganate of potassium yields unsatisfactory results when it is employed as directed by Guyard, its originator, and others. If, however, some salt of an unoxidizable metal, other than potassium or sodium, is added to the solution in which the determination is to be made, the method yields results which are quite accurate.

The reaction, so far as the two manganese compounds are concerned, is as follows: $3MnO + Mn_2O_7 = 5MnO_2$. The neutral and dilute solution of manganese is placed in a long necked flask, acidified with three or four drops of pure nitric acid and about one gram of zinc sulphate added. The solution is then heated to boiling. After which it is treated with permanganate as long as the color disappears. In order to facilitate the subsidence of the precipitate the contents of the flask are vigorously agitated and possibly reheated. The presence of ferric salts in any considerable quantity interferes with the success of the method. These however may be completely removed by addition of oxide of zinc. The author recommends that the value of permanganate solutions to be used in volumetric work be determined by means of a pure manganese salt.

F. Stolba‡ recommends the use of oxalate of lead in standardizing permanganate solutions.

Chromium.—T. Wilm§ finds that chromium oxide, which has been obtained by precipitation of the hydroxide with ammonia, undergoes oxidation when ignited in contact with the air. This oxidation he supposes to be due to the presence of calcium derived from the ammonia.

Lead.—F. Salomon,‖ "The Determination of the Acid in Sugar of Lead and Lead Vinegar."

Platinum.—L. L. de Koninck.¶ "On the Destructibility of Platinum by Fusing Alkaline Carbonates."

Hydrocarbons.—The Testing of Petroleum.**

Hydroxyl Derivatives of Hydrocarbons.—P. Waage,†† "Studies on the Ebullioscope."

Organic Acids, Esters, Salts and their Derivatives.—R. Andreasch‡‡ finds that, when a salt of thioglycolic acid is treated with

* Ber. d. d. ch. Ges. 1879, 1528.
† Liebig's Ann. 198, 318.
‡ Z. an. Ch. 18, 600.
§ Ber. d. d.ch. Ges. 1879, 2223.
‖ Dingler's Journal, 234, 222.
¶ Z. an. Ch. 18, 569.
** Ch. News, 40, 305; Ber. d. d. ch. Ges. 1879, 2184; Dingler's Journal, 234, 52.
†† Z. an. Ch. 18, 417.
‡‡ Z. an. Ch. 18, 601.

a ferric compound and a little ammonia, a dark purple-violet color is produced. On standing the color diminishes, but can be restored by agitating the liquid with air. As a reagent for detecting the presence of ferric compounds this substance exceeds sulphocyanide of potassium in sensitiveness.

L. Claisen,* "A Reaction for Phenylglyoxylic Acid."

B. J. Grosjean,† "On the Determination of Tartaric Acid in Lees and inferior Argol, with some Remarks on Filtration and Precipitation."

H. Schiff,‡ "Determination of Acetyle by Means of Magnesia."

E. Meissl,§ "Investigations on the Adulteration of Commercial Melted Butter."

F. Tschaplowitz,‖ "Apparatus for the Determination of Fats."

F. Soxlet,¶ "The Gravimetric Determination of Milk-Fat."

J. Wolff,** "Separation of Fats and Soaps."

O. Brenken,†† "On the Investigation of Mineral Lubricating Oils."

O. Cailletet,‡‡ "Examination of Olive Oil for Copper."

Carbohydrates.—W. Müller,§§ "Detection of Grape Sugar by Means of Acetate of Copper."

F. W. Pavy,‖‖ "Pavy's Method of Estimating Glucose."

J. Steiner,¶¶ "The Ammoniacal Copper-Test and its Application"—Pavy's method.

P. De P. Ricketts,*** "A Method for the Detection of artificial or dextro Glucose in Cane Sugar, and the exact Determination of Cane Sugar by the Polariscope."

P. Casamajor,††† "On the Influence of Variations of Temperature on the Deviation of Polarized Light by Solutions of Inverted Sugar."

P. Casamajor,‡‡‡ "New Process for the rapid Estimation of Pure Sugar in Raw and Refined Commercial Sugars."

Abeles,§§§ "The Sugar contained by Normal Urine."

J. Seegen,‖‖‖ "On the Supposed Occurrence of Sugar in Normal Urine."

Urea.—C. Méhu¶¶¶ states that when sugar is added to a solution of urea, nearly all the nitrogen is liberated on treatment with hypobromite of sodium.

G. Esbach,**** however, finds that the larger volume of gas obtained when sugar is present is due to a decomposition of the sugar by the hypobromite.

Méhu†††† reaffirms the correctness of his original observations.

E. Drechsel and J. Haycraft,‡‡‡‡ Separation of Urea from Dog's Blood by Dialysis and Subsequent Determination of the same.

* Ber. d. d. ch. Ges. 1879, 1505.
† Jr. Ch. Soc. 1879, 341.
‡ Ber. d. d. ch. Ges. 1879, 1531.
§ Dingler's Journal, 233, 229.
‖ Z. an. Ch. 18, 441.
¶ Dingler's Journal, 232, 461.
** Z. an. Ch. 18, 570.
†† Z. an. Ch. 18, 546.
‡‡ Z. an. Ch. 18, 628.
§§ Z. an. Ch. 18, 600.
‖‖ Chem. News, 39, 249.
¶¶ Ch. News, 40, 139.
*** Jr. Am. Ch. Soc. 1, 2.
††† Jr. Am. Ch. Soc. 1, 26.
‡‡‡ Jr. Am. Ch. Soc. 1, 205.
§§§ Ber. d. d. ch. Ges. 1879, 1704.
‖‖‖ Ber. d. d. ch. Ges. 1879, 1705.
¶¶¶ Comptes rendus, 89, 175.
**** Comptes rendus, 89, 417.
†††† Comptes rendus 89, 486, 616.
‡‡‡‡ Jr. prak. Ch. 19, 334.

Alkaloids.—J. Tattersall,* "A New Test for Papaverine."

A Poehl,† On Distinguishing Atropin from Daturine.

Glénard,‡ On Distinguishing Quinine from Cinchonine.

H. Ranke,§ Experiments on the Detection of Strychnine in the decomposing Cadaver.

F. Selmi,‖ On the Alkaloids of the Cadaver.

A. Loesch,¶ "On the quantitative Determination of the Alkaloids of Plants."

Miscellaneous.—F. Fischer,** "On the Investigation of Atmospheric Air."

W. Van Slooten,†† "Analysis of Air."

Ira Remsen,‡‡ "Organic Matter in the Air."

G. Aarland,§§ "Analysis of Ores and Furnace Products."

A. Terreil,‖‖ "Analysis of some metallic Fragments from Peruvian Graves."

F. Mauro,¶¶ "An Analysis of Spinel."

Maumené,*** "On the Composition of Slate."

A. Smethan,††† "Composition of a Boiler Incrustation."

D. Playfair,‡‡‡ "On the Detection of some rare Metals in Pyrites Flue-Dust."

C. Zimmermann,§§§ "On the Separation of the heavy Metals of the Sulphide of Ammonium Group."

B. Corenwinder and G. Contamine,‖‖‖ "A new Method of Analyzing with Precision the Potashes of Commerce."

E. F. Smith,¶¶¶ "New Results in Electrolysis."

C. J. H. Warden,**** "Analysis of Poppy Petal Ash."

S. F. Peckham,†††† "On the Composition of the Ashes of Wheat-Bran burned under a Steam Boiler."

L. Ricciardi,‡‡‡‡ "Analysis of Tobacco."

G. Stein,§§§§ "On the Analysis of Turkey-Red."

A. W. Blythe,‖‖‖‖ "The Composition of Cow's Milk in Health and Disease."

W. H. Watson,¶¶¶¶ "On the Detection of Milk Adulteration."

F. Becker,***** "Examination of Beeswax."

M. Buchner,††††† "On the Adulteration of Beeswax."

J. M. Eder,‡‡‡‡‡ "The Examination and the Properties of Chinese Tea."

C. Husson,§§§§§ "A Study of Tea, Coffee and Chiccory."

* Chem. News 40, 126.
‡ Z. an. Ch. 18, 629.
Z. an. Ch. 18, 506.
** Dingler's Journal 234, 46.
†† Bull. National Board of Health, Jan. 31, 1880.
‡‡ Bull. de la Soc. chim. 31, 151.
*** Comptes rendus, 89, 423.
††† Chem. News 39, 245.
‡‡‡ Comptes rendus, 89, 907.
**** Chem. News 39, 27.
†††† Ber. d. d. ch. Ges. 1879, 683.
‡‡‡‡ Jr. Chem. Soc. 1879, 530.
***** Ber. d. d. ch. Ges. 1879, 2099.
†††††‡‡‡‡‡ Dingler's Journal 231, 445, 526.

† Z. an. Ch. 18, 628.
‖ Z. an. Ch. 18, 635.
¶ Chem. Centralblatt 1879, 812, 826.
†† Jr. Am. Ch. Soc. 1, 263.
‖‖ Ber. d. d. ch. Ges. 1879, 270.
¶¶ Ber. d. d. ch. Ges. 1879, 685.
††† Chem. News 39, 236.
‖‖‖ Lieb. Ann. 199, 1.
¶¶¶ This Journal 1, 329.
†††† Chem. News 39, 244.
‖‖‖‖ Ber. d. d. ch. Ges. 1879, 1174.
¶¶¶¶ Ch. News 40, 102.
††††† Dingler's Journal 231, 272.
‖‖‖‖§§§§§ Ann. de Chim. [5] 16, 419.

Means of Detecting the Adulteration of Saffron.*

D. Lindo,† "Examination of Caoutchouc Goods."

J. M. Kostersitz and F. Hess,‡ "On the Valuation of Explosives."

D. Vitali and H. Schiff,§ "Examination of old Blood."

H. R. Proctor,‖ "Determination of the free Acid in Tan Liquors."

A. Houzeau,¶ "On Gravivolumetry."

F. Salomon,** "Quantitative Determination of Colored Acids."

G. Williams,†† "On the new Substitute for Litmus."

A. H. Allen,‡‡ "Normal Solutions."

F. A. Gooch,§§ "On a new Method for the Separation and Subsequent Treatment of Precipitates in Chemical Analyses."

K. Kraut,‖‖ "On Filter-paper and Filtration."

R. Popper,¶¶ "Quantitative Determination of Precipitates without Filtering, Washing or Drying the same."

J. H. Poynting,*** "On the Estimation of small Excesses of Weight by the Balance from the time of Vibration and the Angular Deflection of the Beam."

H. N. MORSE.

NOTES.

Synthesis of Formic Acid.

V. MERZ and J. TIBIRIÇA sum up the results of an elaborate investigation on the action of carbon monoxide on alkalies with these statements:

Carbon monoxide is absorbed by caustic alkalies at about 200°, and a salt of formic acid is produced.

In order to saturate caustic soda as thoroughly as possible, it should be used in the form of soda-lime; this should be very porous, the gas should be moist, and the temperature not above 220°.

As the absorption of carbon monoxide takes place rapidly when the proper precautions are observed, formic acid, or formates, may best be prepared on the large scale from inorganic material.

According to the information furnished in Wagner's Jahresbericht, formic acid appears to be used principally in the manufacture of certain esters. But it would now be interesting to de-

* Chem. News, 39, 35
† Chem. News 39, 99.
‡ Z. an. Ch. 18, 623.
§ Ber. d. d. ch. Ges. 1879, 684.
‖ Chem. News 39, 246.
¶ Comptes rendus 88, 747.
** Dingler's Journal 234, 317.
†† Chem. News 39, 98.
‡‡ Chem. News 40, 239.
§§ This Journal 1, 317.
‖‖ Z. an. Ch. 18, 543.
¶¶ Z. an. Ch. 18, 14.
*** Chem. News 39, 45.

termine how far this acid may be used for technical purposes in place of acetic acid, and also as a reducing agent. It should further be remarked that according to Jodin* free formic acid is an antiseptic, and under some conditions is superior to phenol in this respect.—(*Ber. d. deutsch. chem. Gesell.* 13, 23.)

The Valence of Boron.

Nearly all the known compounds of boron can be explained on the assumption that the element is trivalent. Two compounds have been described, however, which indicate that boron may, under some circumstances, play the part of a quinquivalent element. These are an ester prepared by Frankland, to which he gives the formula $B_2(C_2H_5)(OC_2H_5)_4$, and an oxychloride $BOCl_3$ prepared by C. Councler. A. MICHAELIS and P. BECKER have now shown that, if a phenyl derivative of the trichloride of boron be first prepared, according to the following equation:

$$2BCl_3 + Hg(C_6H_5)_2 = 2C_6H_5BCl_2 + HgCl_2,$$

this substance readily takes up chlorine. A product is formed which is called *phenylboron tetrachloride*, $C_6H_5BCl_4$. This corresponds to similar derivatives obtained from phosphorus and arsenic, and makes it very probable that boron may be either trivalent or quinquivalent.—(*Ber. d. deutsch. chem. Gesell.* 13, 58.)

Artificial Alkaloids.

A. LADENBURG continues his interesting studies of the alkaloids. He finds that the atropine obtained by him in treating the tropate of tropine with dilute hydrochloric acid is identical with natural atropine. He has, further, treated other salts of tropine in the same way, and thus obtained representatives of a class of artificial alkaloids to which he gives the generic name *tropeines*. The three substances of this class described are made from the salicylate, oxytoluate and phthalate of tropine. Oxytolutropeine acts upon the human pupil almost as energetically as atropine. It has been used extensively in the ophthalmological clinic, and the conclusion drawn from the experiments thus far performed is that in many cases it is to be preferred to atropine.—(*Ber. d. deutsch. chem. Gesell.* 13, 104.)

On the new Hydrogen Lines and the Dissociation of Calcium.

H. W. VOGEL has photographed the spectrum of pure hydrogen, evolved by electrolysis, and finds certain new lines, among which the most striking is one which is almost coincident with the line H′ (Frauenhofer) usually attributed to calcium. This is called the *fifth principal hydrogen line*. The discovery of this new line of hydrogen is of interest in connection with Lockyer's supposition

* Wagner, Jahresbericht, 1866, 287, and Zeitschrift f. Chem. 1866, 95.

that calcium is dissociated at a very high temperature. Lockyer has suggested that when calcium is dissociated it is broken up into two bodies, X and Y, and that the first H line belongs to one of these and the second line to the other. Huggins has shown that of the two thick H-lines of the solar spectrum only the first is present in the spectra of Sirius and Vega. According to Lockyer, this isolated line is due to the presence of one of the components of dissociated calcium. Vogel, on the other hand, believes that it is the fifth hydrogen line, and has consequently no connection with calcium. Lockyer has, further, called attention to an observation made by Young, according to which the H′-line was seen to be injected into the chromosphere 25 times and the H″-line 50 times. The appearance of the H′-line alone is explained on the supposition that it is due to dissociated calcium. But Vogel believes that the H′-line seen alone was the fifth hydrogen line.—(*Ber. d. deutsch. chem. Gesell.* 13, 274.)

Chlorine, Bromine and Iodine at High Temperatures.

VICTOR MEYER* and J. M. CRAFTS† have shown that when pure chlorine is heated to yellow heat its density is not changed, as it is when produced in the nascent state. It seems quite impossible, at present, to furnish a satisfactory explanation for this difference between free and nascent chlorine.

Meyer has communicated some details in regard to the density of iodine at high temperatures. He shows that at 800° there is a marked decrease in the density, and, from about 1027 to 1567°, it remains unchanged and is exactly equal to the value calculated for $\frac{2}{3}Cl_2$.

Crafts,‡ however, finds that the density of iodine vapor does not remain unchanged after the value corresponding to the formula $\frac{2}{3}Cl_2$ is reached, but that there is a still further decrease.

THE chair of chemistry in the newly established Agricultural College of Berlin, is to be filled by PROF. H. LANDOLT, of Aix-la-Chapelle, well-known by his exhaustive studies on the relations between the optical properties of bodies and their chemical constitution. His wide experience in saccharimetry has likewise led to his simultaneous appointment as director of the chemical laboratory established at Berlin by the German *Verein für Rübenzucker-Industrie*. Prof. Landolt is succeeded in the Polytechnic of Aix-la-Chapelle by PROF. A. CLASSEN, who has recently published two favorably received laboratory manuals on Qualitative and Quantitative Analysis.—(*Nature.*)

* Berichte d. deutsch. chem. Gesell. 13, 399. † Compt. rend. 90, 183.
‡ Compt. rend. 90, 690.

IT is proposed to commemorate, by a permanent memorial, the distinguished services rendered to science and education by DR. THOMAS ANDREWS, during the thirty years that he was occupant of the chair of chemistry in the Queen's College, Belfast.

THE French chemist, SAINTE-CLAIRE DEVILLE, has resigned the professorship at the École Normale of Paris which he has held for twenty-nine years. He is succeeded by L. TROOST, who has long been well-known for his careful investigations in the field of inorganic chemistry.

M. ZININ, the well-known Russian chemist, recently died at St. Petersburg. One of his chief discoveries was the conversion of nitro- into amido-compounds. One of the first substances made in this way was aniline.

PAUL MENDELSSOHN BARTHOLDY, a son of the composer, and himself a chemist well-known in connection with chemical industry, recently died in Berlin. He was a member of the firm of Martius & Mendelssohn of Berlin, manufacturers of aniline and aniline colors.

PROF. JAMES M. CRAFTS has recently been awarded a prize by the French Academy of Sciences for his researches in the field of organic chemistry.

PROF. A. R. LEDOUX, Director of the North Carolina Agricultural Experiment Station, has resigned.

PROF. GEORGE A. SYMTH, of the University of Vermont, has left his professorship and engaged in work in connection with sanitary chemistry at Newport.

RECENT PUBLICATIONS RELATING TO CHEMISTRY.

I. – ENGLISH.

BLOXAM, C. L. Chemistry, Inorganic and Organic, with Experiments. 4th Edition. London: Churchill. 16s.

CLOWES, F. Elementary Treatise on Practical Chemistry and Qualitative Analysis. 3d Edition. London: Churchill. 7s. 6d.

EAGLE, J. A Note-book of Solubilities, arranged chiefly for the use of Prescribers and Dispensers. London: Lewis. 2s. 6d.

FRANKLAND, E. Water Analysis for Sanitary Purposes. With Hints for the Interpretation of Results. London: Van Voorst. 5s.

JARMAIN, G. Systematic Course of Qualitative Analysis, arranged in Tables. 4th Edition. London: Longmans. 1s. 6d.

PERCY, J. Metallurgy: the Art of Extracting Metals from the Ores. Silver and Gold, Part I. London: Murray. 30s.

ROBINSON, H. Sewage Disposal. London: Spons. 4s.

TILDEN, W. A. Practical Chemistry: the Principles of Inorganic Analysis. London: Longmans. 1s. 6d.

II.—FRENCH.

GIRARDIN, J. Leçons de chimie élémentaire appliquée aux arts industriels. 6e Ed. Supplement aux 5 vol. Masson. 5fr.

III.—GERMAN.

ARTUS, F. W. Grundzüge der Chemie in ihrer Anwendung auf das praktische Leben. Wien: Hartleben. M. 6.00.

DAMMER, O. Kurzes chemisches Handwörterbuch. Berlin: Oppenheim. M. 17.00.

EPPINGER, O. Ueber die Einwirkung des Aethyl- und Diaethylamins auf Aceton. Halle-Wittenberg.

FISCHER. Die chemische Technologie des Wassers. Braunschweig: Vieweg und Sohn. M. 11.60.

HEMPEL. Neue Methode zur Analyse der Gase. Braunschweig: Vieweg und Sohn. M. 5.00.

JACOBSEN. Die chemische Industrie. 3 Jahrg. Berlin: Springer. M. 20.

JAHRESBERICHT über die Fortschritte auf dem Gesammtgebiete der Agricultur-Chemie. Begründet v. R. Hoffmann, fortgeführt v. A. Hilger. Das Jahr 1878. Berlin: Springer. M. 22.00.

LORSCHEID, J. Lehrbuch der anorganischen Chemie nach den neuesten Ansichten der Wissenschaft. 8 Aufl. Freiburg: Herder. M. 4.40.

MAERCKER, M. Die Kalisalze und ihre Anwendung in der Landwirthschaft. Berlin: Wiegand, Hempel und Parey. M. 3.00.

MUSPRATT'S theoretische, praktische, und analytische Chemie in Anwendung auf Künste und Gewerbe. Frei beiarb. v. B. Kerl und F. Stohmann. 3 Aufl. 7 Bd. 25, 26, 27, 28 Lfg. Braunschweig: Schwetschke u. Sohn. à M. 1.20.

PERNTZ. Die Industrie der Mineralöle, des Petroleums, Paraffins, und Ceresins nebst den neuesten Fabrikationsmethoden. Wien: Gerold's Sohn. M. 6.00.

REVERDIN, F. UND E. NÖLTING. Ueber die Constitution d. Naphthalins und seiner Abkömmlinge. Basel: Georg. M. 3.20.

v. RICHTER, V. Chemie der Kohlenstoffverkindungen, oder organische Chemie. 2 Aufl. Bonn: Max Cohen u. Sohn. M. 11.00.

SACHSE, R. Phytochemische Untersuchungen. Leipzig: Voss. M. 4.00.

SIEGMUND, F. Die Wunder der Physik und Chemie. Wien: Hartleben.

TRENNUNGS-METHODEN, chemische. Graz: Leuschner und Lubensky. M. 1.00.

WINKLER, C. Anleitung zur chemischen Untersuchungen der Industrie-Gase. I. Abtheilung: Qualitative Analyse. II. Abtheilung: Quantitative Analyse. Freiberg.